

REVIEW OF NAVY PROGRAM TO DEVELOP OPTICAL QUALITY DIAMOND WINDOWS AND DOMES

Daniel C. Harris*

Naval Air Systems Command, China Lake, California

Abstract: From 1989 to 2000, the U.S. Navy sponsored research and exploratory development programs to make optical quality chemical vapor deposited diamond and to learn its properties. This paper recounts the development of optical quality diamond and discusses the properties and fabrication capabilities that were achieved. In the year 2002, there exists a commercial capability for optical quality diamond, but the price keeps it out of the hands of all but a few potential users.

A LITTLE HISTORY

It has been known for decades that Type IIa natural diamond possess unique properties for durable optical windows. For example, the Pioneer spacecraft that entered the atmosphere of Venus in 1978 had a radiometer window made from a single crystal of diamond with a diameter of 18.2 mm and a thickness of 2.8 mm. This 13-carat diamond was required to survive high pressure (90 atm), high temperature (800 K), and a corrosive atmosphere (sulfuric acid), and to transmit radiation with wavelengths from 3 to 150 μm .^{1,2} Natural diamond could be considered for use as a window only in an exotic application for which the required size was not too large and price was almost no obstacle.

Prospects for diamond windows changed dramatically in the 1980s when gas-phase processes for depositing polycrystalline diamond over large areas at moderate temperature (1000°C) were discovered. It became conceivable that windows with dimensions of several centimeters could be fabricated at reasonable cost for military sensors.

The first recorded synthesis of diamond³ by chemical vapor deposition (CVD) occurred in 1952 when William Eversole of Union Carbide deposited new layers of carbon atoms (diamond) on the surface of natural diamond seed crystals.⁴ The carbon was obtained by decomposing CO or CH₄ at 900–1100°C. After a period of growth, nondiamond carbon (graphite) was removed by etching with 50 atm of H₂ at 1000°C.

* Code 4T42A0D, 1 Administration Circle, Naval Air Systems Command, China Lake CA 93555;
Phone 760-939-1649; harrisdc@navair.navy.mil.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 00 MAY 2002		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Review Of Navy Program To Develop Optical Quality Diamond Windows And Domes				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Air Systems Command, China Lake CA 93555				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM201579., The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Work begun in the 1950s led by Boris Derjaguin and Boris Spitsyn at the Institute of Physical Sciences in Moscow also deposited diamond on diamond seeds by chemical vapor deposition from CBr_4 , Cl_4 and CCl_4 sources.³ In the late 1960s Spitsyn observed accelerated diamond growth from CH_4 in the presence of H_2 at 1000°C . Although the Soviet work was reported in numerous technical publications, and even in *Scientific American*,⁵ growth rates were so small and the method so impractical that chemical vapor deposition of diamond attracted little attention. Around the same time, John Angus at Case Western Reserve University was also depositing diamond onto diamond seeds from CH_4 in the presence of H_2 .⁶ He increased the mass of seed crystals by up to 24% by repeated cycles of deposition and etching away non-diamond carbon with 50 atm of H_2 at 1033°C . In 1971 Angus suggested that atomic hydrogen formed by dissociation of H_2 at 1000°C played a critical role in diamond deposition, though that role was not known.³

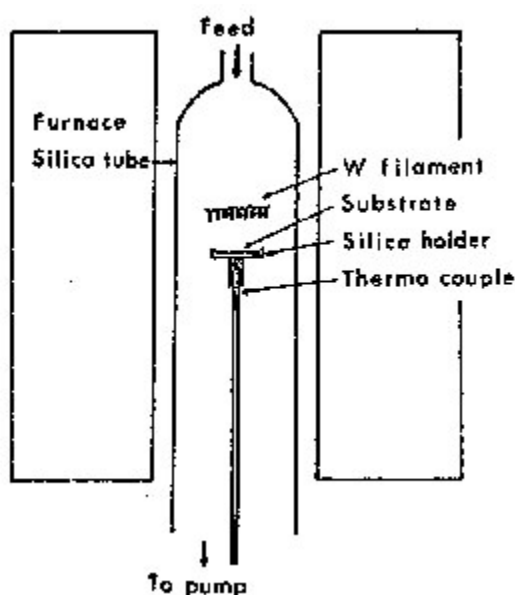


Figure 1. Hot-filament apparatus used in Japan to grow diamond films at $\sim 900^\circ\text{C}$.

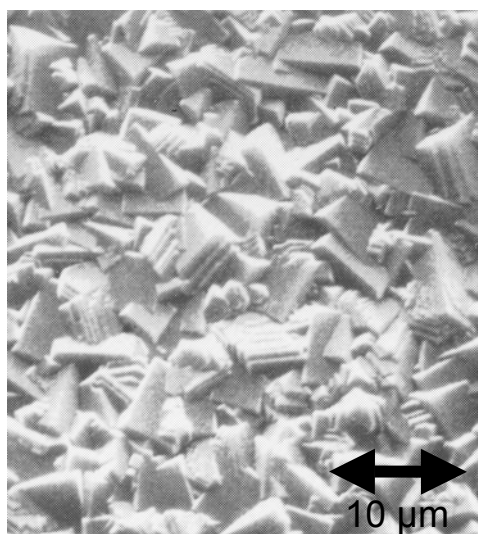


Figure 2. Representative microstructure of CVD diamond film.

In the 1970s, Japanese workers at the National Institute for Research in Inorganic Materials began intensive research into finding a more practical route to synthetic diamond. Beginning in 1982, Seiichiro Matsumoto, Nobuo Setaka, and coworkers published a series of papers on the chemical vapor deposition of diamond onto nondiamond substrates (such as silicon and tungsten) using a hot filament to dissociate the CH_4/H_2 gas (Figure 1).⁷ An important extension of the technique was reported by Yukio Saito and coworkers who found that a microwave plasma could be used in place of a hot filament to decompose the CH_4/H_2 mixture for diamond deposition.⁸

Although the Japanese were rapidly improving the process of diamond deposition and publishing their results, a firsthand account of their progress by Rustum Roy of Pennsylvania State University was required to ignite a major effort on chemical vapor deposition of diamond in the U.S.³ Roy visited Japan and the Soviet Union in 1985 and came back with reports of diamond being grown with significant size and quality. His reports and lobbying efforts resulted in major

government programs with universities and industry to explore and exploit the new diamond technology. At the same time, many laboratories in Europe and around the world initiated intensive research into diamond deposition. The genie was out of the bottle.

Preceding the major U.S. initiative on diamond, General Electric Co., which invented the high-temperature, high-pressure process for making diamond in 1954, reactivated its long dormant effort in chemical vapor deposition. Led by Thomas Anthony and Robert DeVries, General Electric developed and patented a method for making diamond by hot-filament deposition of CH_4/H_2 onto a molybdenum substrate.⁹ Since 1992, based on its patents, General Electric Co. claimed all U.S. rights to “substantially transparent diamond films having a thickness of at least 50 microns” and offered to license its technology for commercial applications.

OPTICAL QUALITY DIAMOND FILMS

From 1984 to 1989, the Materials Division of the Office of Naval Research (ONR) sponsored an Accelerated Research Initiative intended to improve the erosion resistance and thermal shock resistance of long wave (8-14 μm) infrared materials. Comprised mainly of university research efforts, with some projects in industrial and government labs, this effort explored a wide variety of materials and microstructures that could have improved performance, but none promised any overwhelming advantages. When reports of CVD diamond began to appear in the literature, it was quickly recognized as a revolutionary optical material. Some effort in the research initiative was redirected toward CVD diamond to see if it could be made with optical quality and to see how the properties of CVD material would compare to the known properties of Type IIa natural diamond.

Table 1 compares properties measured for CVD diamond in the mid 1990s to those of zinc sulfide and sapphire, which are widely used long wave and midwave window materials, respectively. Being the hardest known material, diamond is much harder than zinc sulfide or sapphire. Hardness correlates with resistance to abrasion by sand particles, giving diamond orders of magnitude greater resistance than other materials to sand abrasion in the field. Diamond has the highest thermal conductivity of any material at or above room temperature (5 times greater than copper), so it has exceptional resistance to thermal shock failure. The thermal shock figure of merit for diamond in Table 1 is ~100 times greater than those of zinc sulfide or sapphire, meaning that diamond can withstand ~100 times the heat flux of the other materials without shattering. Diamond is also a better microwave-transmitting material than zinc sulfide or sapphire because of the lower dielectric constant of diamond. Low dielectric constant translates into low reflection losses.

Once diamond was identified as a viable infrared window material, new programs were organized for the period 1989-1994. A new Accelerated Research Initiative sponsored work at Auburn University, BNR Europe, Caltech, Cambridge University, Cornell University, the University of Florida, Harvard, Howard University, General Motors Research Laboratory, Northwestern University, Pennsylvania State University, Rice University, Rockwell Science Center, Stanford University, the National Institute of Standards and Technology, and the Naval Air Warfare Center, China Lake. A major thrust was to learn the mechanism of diamond growth so that the process might be optimized.

Table 1
Comparison of Properties of Diamond to Those of Other Infrared Window Materials

Property	CVD Diamond	Zinc Sulfide*	Sapphire
Transmission			
Ultraviolet	✓ [‡]	no	✓
Visible	✓ [‡]	MS grade only	✓
Near infrared (1-2 μm)	✓	MS grade only	✓
Midwave infrared (3-5 μm)	thin layer	MS grade only	✓
Long wave infrared (8-14 μm)	only	✓	no
Microwave	✓	high reflection	high reflection
	✓		
Hardness (kg/mm^2)	9000	160-250	2200
Mechanical strength (MPa)	≥ 200	70-100	$\sim 300-700$
Thermal expansion coefficient (10^{-6} K^{-1})	1	7	6
Thermal conductivity ($\text{W/m}\cdot\text{K}$)	2300	19-27	36
Thermal shock figure of merit (10^3 W/m)	380	3	4
Microwave dielectric constant	5.7	8.35	9.39 ($E \parallel c$) [†] 11.58 ($E \perp c$)
Microwave loss tangent at 35 GHz	< 0.00015	0.0024	0.00005 ($E \parallel c$) [†] 0.00006 ($E \perp c$)

[‡]CVD diamond has significant optical scatter at visible and ultraviolet wavelengths. Type IIa natural diamond has low scatter and excellent transmission at these wavelengths.

*MS grade is multispectral grade marketed under the tradenames Cleartran and Waterclear. The range of properties given for zinc sulfide are for standard and multispectral grades.

[†]Dielectric properties for sapphire are parallel and perpendicular to the c axis of the crystal.

One example of a significant accomplishment of the research initiative is shown in Figure 3. Work by Stephen Harris of General Motors and David Goodwin of Caltech led to a unified mechanism for diamond growth without adjustable parameters that agreed with observed growth rates varying over 2 orders of magnitude in reactors that utilized rf or dc plasma torches, flames at low and high pressure, and hot filaments.¹⁰ In the proposed mechanism, a hydrogen atom is removed from the H-terminated surface of diamond by gaseous H atoms. A gaseous CH_3 group then adds to either a “dimer” or “trough” site on the crystal surface, the latter site being rate determining. Further hydrogen abstraction is required to complete the process of adding a carbon atom to the crystal.

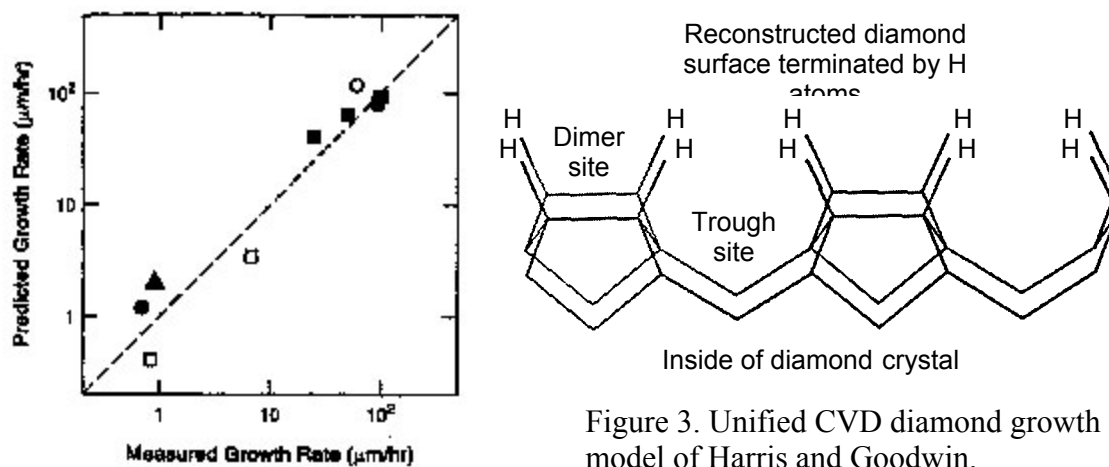


Figure 3. Unified CVD diamond growth model of Harris and Goodwin.

In parallel with the ONR research program was an ONR exploratory development program. In the period 1989 to 1994, the development effort had contracts at Westinghouse, Raytheon, Texas Instruments, Norton, Rocketdyne, Auburn University, and General Research Corp. There were also substantial collaborations with the Naval Research Laboratory, Oak Ridge National Laboratory, the Johns Hopkins University Applied Physics Laboratory, Colorado State University, and the British Defence Research Agency.

Work at Westinghouse from 1990-1993 was intended to (1) demonstrate growth of optical quality diamond films (up to $\sim 10\text{-}20\text{ }\mu\text{m}$ thick) by microwave plasma deposition, (2) demonstrate “optical brazing” of diamond to flat and curved surfaces of ZnS and ZnSe up to 38 mm in diameter, and (3) evaluate the rain erosion resistance of coated windows. The key to optical brazing in Figure 4 is to hot press the rough growth surface of a diamond film with an arsenic-selenium-sulfur glass whose refractive index matches that of diamond.^{11,12} The glass fills in the rough diamond surface (Figure 2) and eliminates optical scatter that would otherwise arise from the rough surface (Figure 5). The glass also binds the diamond to the zinc sulfide or zinc selenide window. After brazing, the silicon substrate on which the diamond was grown is etched away with acid, exposing a smooth diamond surface.

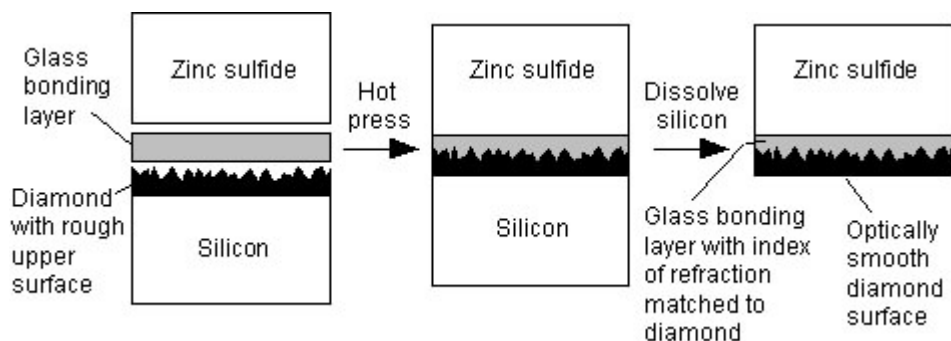


Figure 4. Westinghouse optical brazing process for attaching diamond film to zinc sulfide or zinc selenide. The refractive index of the As:Se:S glass is matched to that of diamond to reduce optical scatter from the rough diamond surface to a negligible level.

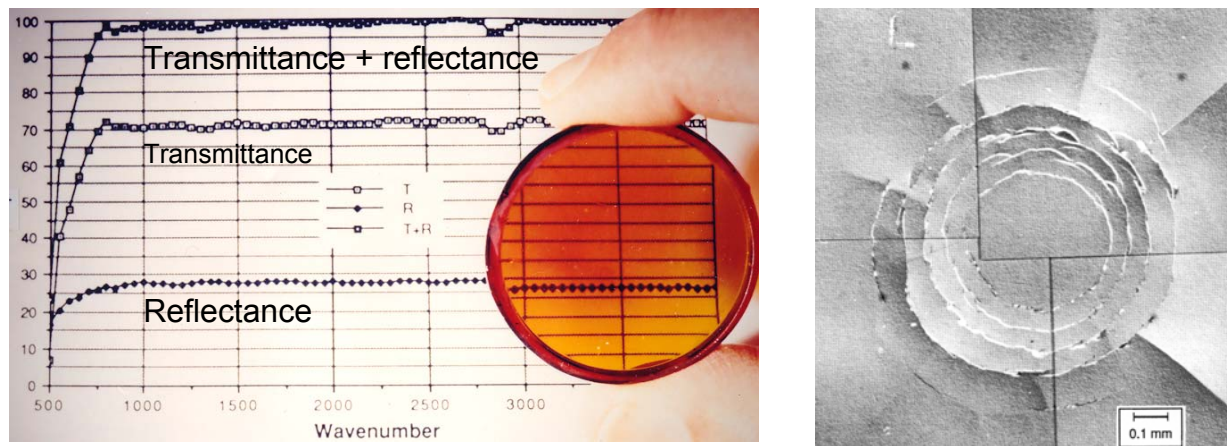


Figure 5. *Left:* 8-μm-thick diamond film optically brazed to 38-mm-diameter zinc selenide window. Transmittance plus reflectance sum to ~99% through most of the infrared region. *Right:* Waterdrop (1.75 mm diameter) impact on 20-μm-thick diamond film brazed to zinc selenide and impacted at 432 m/s (Mach 1.25).

Single-drop water impact tests at General Research Corp. showed that a 20-μm-thick diamond film brazed to zinc selenide or zinc sulfide approximately doubled the damage threshold velocity for 2-mm-diameter drops. Coated ZnSe exhibited a damage threshold of Mach 1.0 and coated ZnS had a threshold of Mach 0.9. Initial damage was circumferential fracture of the diamond coating (Figure 5). Above the threshold velocity, the coating provided no additional protection against damage in the window material. Doubling the diamond thickness to 40 μm slightly *lowered* the damage threshold velocity. Increasing the thickness of the braze layer from a few microns up to 18 or 35 μm was also not productive, with an increasing tendency toward formation of radial fractures.

Eventually, the Navy gave up on the idea of coating a missile dome with diamond because of the large difference in thermal expansion between diamond and the underlying material (Table 1). In the case of diamond on a zinc sulfide dome, Figure 6 shows an exaggerated view of the dome expanding more than the coating in a likely catastrophic manner. Also, the thin diamond coating is not expected to provide substantial protection of the underlying material against thermal stress.

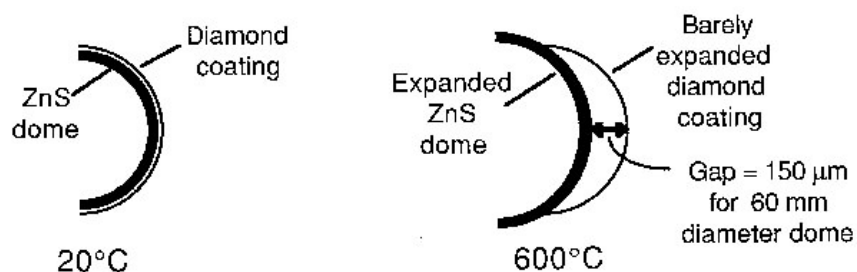


Figure 6. Thermal expansion mismatch of a diamond coating on a zinc sulfide dome is expected to lead to delamination and optical defocus when the assembly is heated.

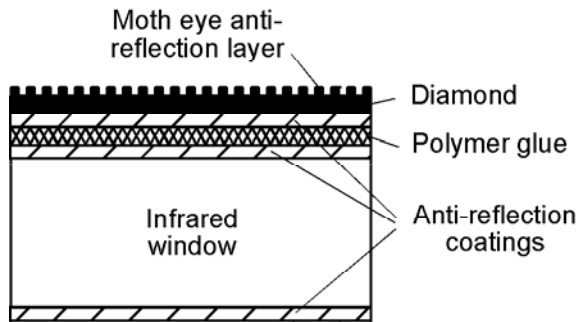


Figure 7. Polymer glue attachment of diamond to an infrared window.

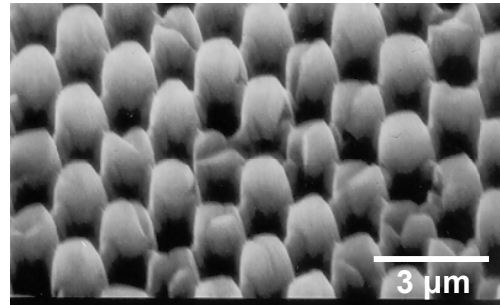


Figure 8. All-diamond moth eye structure from Rockwell Science Center.

For systems that would not undergo large temperature excursions, a diamond coating has merit. The Air Force therefore carried out an extensive study of diamond (and other) coatings on sensor windows. In addition to optical brazing, an infrared-transparent polymer glue was found to be good for attaching hard, impact resistant claddings to windows Figure 7).¹³ The soft glue layer reflects stress waves from impacts back into the diamond layer, rather than down into the window.¹⁴ The proprietary glue is only useful up to $\sim 150^{\circ}\text{C}$. The outer layer of Figure 7 illustrates a “moth eye” antireflection layer on top of diamond.¹⁵ An actual moth eye surface made of diamond is shown in Figure 8. Small diamond projections from the surface effectively grade the refractive index between that of diamond and that of air, to reduce reflection from the surface. The diamond projections are analogous to the projections from the wall of an anechoic chamber for radar measurements.

OPTICAL QUALITY BULK DIAMOND

A year after initiating work on thin layers of optical quality diamond, the ONR exploratory development program decided that bulk diamond windows and domes with a thickness of ~ 1 mm held the solution to thermal shock resistant sensor windows. Three parallel contracts with Raytheon Research Division, Texas Instruments, and Norton Co. had the following goals:

- Phase I. (1991-1992) Deposit optical quality diamond with a thickness of 1 mm. Measure optical properties, mechanical strength, and erosion resistance.
- Phase II. (1993) Measure mechanical strength and erosion resistance of antireflection-coated diamond disks. Fabricate prototype diamond domes with a diameter of 25 mm and thickness of 1 mm.
- Phase III. (1994) Fabricate a 60-mm-diameter, antireflection-coated diamond dome (1 mm thick). Measure microwave transmission properties of CVD diamond.

Raytheon chose to compare diamond deposition from a hot-filament reactor and a microwave plasma reactor. Figure 9 shows a hot-filament reactor configured for dome growth. Lower infrared optical absorption and greater thermal conductivity showed that the microwave plasma produced higher quality diamond, so all of Raytheon’s work shifted to microwave plasma by 1993. Raytheon then built a series of custom-designed 915 MHz reactors to create a plasma ball large enough to deposit diamond over a diameter of 125 mm.

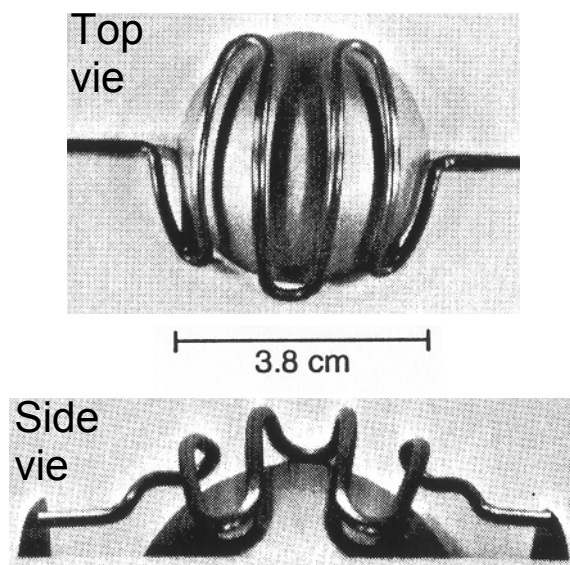


Figure 9. Arrangement of filament for growing diamond on a dome-shaped mandrel at Raytheon.

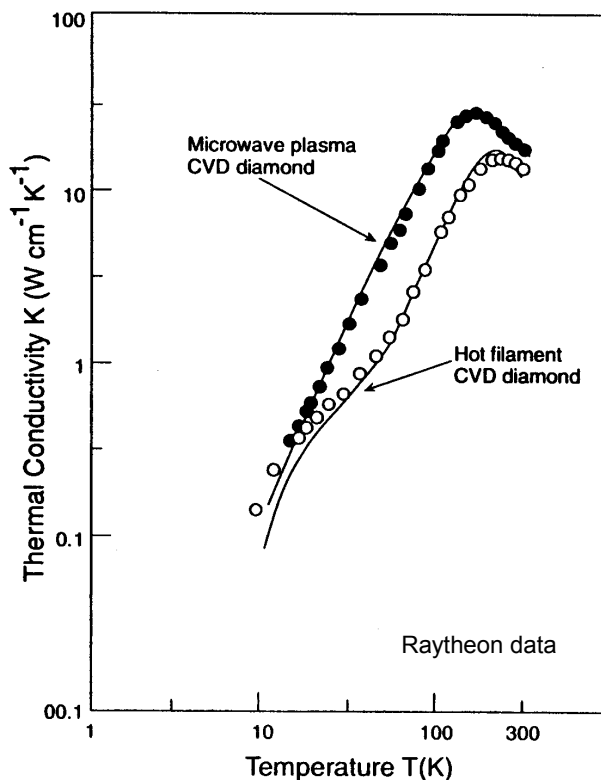


Figure 10. Comparison of thermal conductivity of diamond films grown by microwave plasma and by hot-filament.

Texas Instruments began making diamond with a direct current plasma torch¹⁶ and did extensive work to optimize growth rate and quality. By 1994 Texas Instruments joined forces with Olin Aerospace Co. to bring on line a supersonic hydrogen arc jet, which was originally designed as an ion engine for interplanetary space travel. Figure 11 shows three ion engines ganged together for growth of hemispheric domes with a diameter of 60 mm.¹⁷ A fairly uniform deposit of white-colored diamond could be grown with this reactor (Figure 12). One important finding from Texas Instruments was that the optical quality of the grains in the polycrystalline CVD diamond was better than the optical quality of the grain boundaries (Figure 13). As is generally true of polycrystalline optical ceramics, large-grain material, having less of a fraction of grain boundaries, is likely to be of higher optical quality than small-grain material.

Norton Co. had a major effort in diamond before the Navy expressed interest in optical diamond. Norton was making diamond cutting tool inserts and diamond coatings for cutting tools. Cutting tools require high mechanical strength best afforded by small-grain, "black" diamond. Norton built a magnetically mixed arc jet reactor capable of giving a uniform deposit over a diameter of ~100 mm. To grow optical quality diamond, conditions were modified for slow growth rate. To our knowledge, nobody has yet demonstrated growth of good optical quality diamond at linear growth rates much above 3 $\mu\text{m}/\text{h}$, and often the rate is closer to 1 $\mu\text{m}/\text{h}$. Figure 14 shows the improvement in optical quality of diamond deposited at Norton between 1990 and 1993.

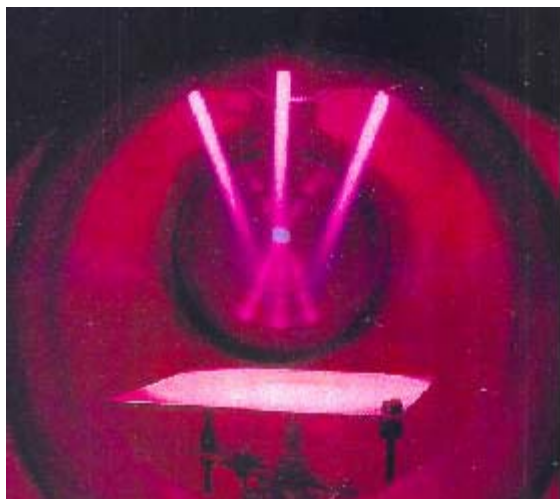


Figure 11. Three supersonic hydrogen arc jets (ion engines designed for spacecraft) ganged together to grow diamond over areas as large as 200 mm (Texas Instruments).



Figure 12. Uniform diamond dome (60 mm diameter $\times$ 0.7 mm thick) grown by Texas Instruments in 1994 with the reactor shown in Figure 11.

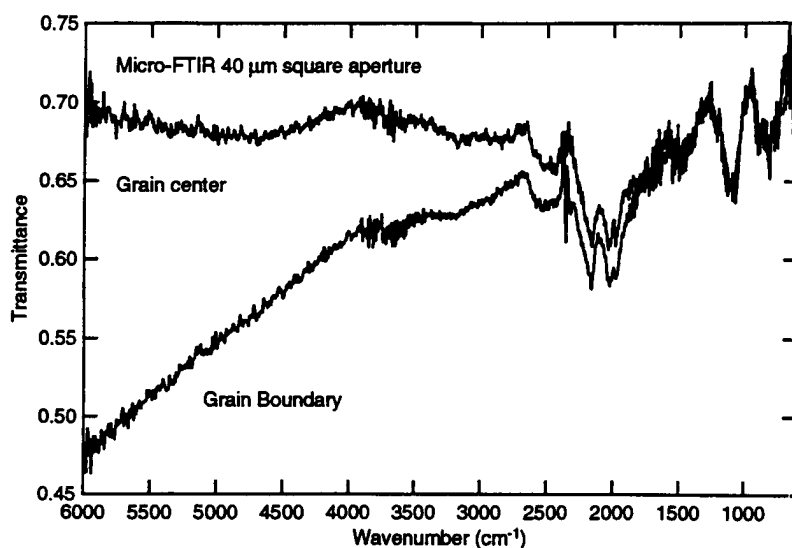


Figure 13. Infrared transmission loss in CVD diamond arises mainly from grain boundaries [Texas Instruments data].

By 1993, optical quality CVD diamond had been grown in thicknesses up to 1 mm and diameters of 25 mm and the following properties had been achieved:¹⁸

- Long wave (8-12 μm) infrared emittance less than 3%
- Long wave infrared optical scatter less than 1%
- Thermal conductivity and thermal expansion equivalent to those of Type IIa diamond
- Microwave dielectric constant of 5.7 (equal to Type IIa diamond) and loss tangent 0.0002
- Survives in air up to 700°C before combustion begins
- Thermal shock resistance 100 times greater than sapphire

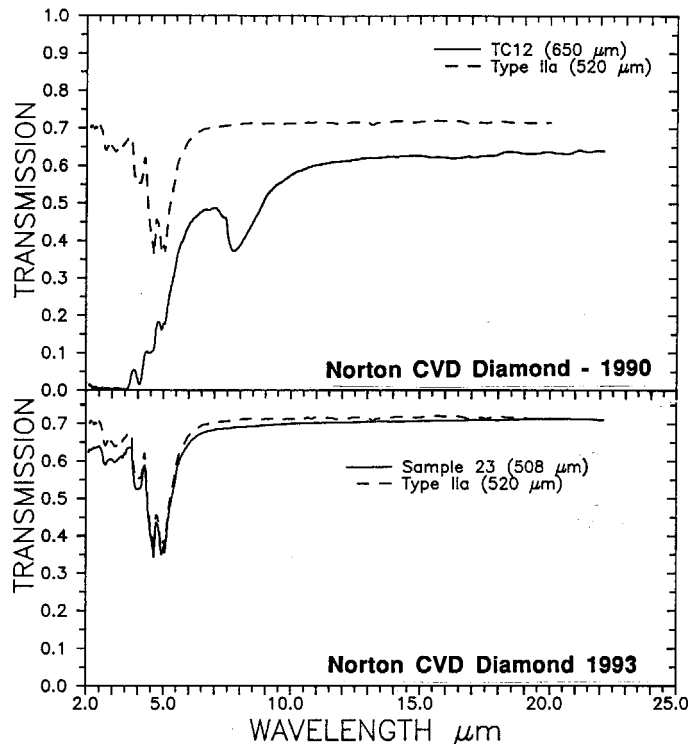
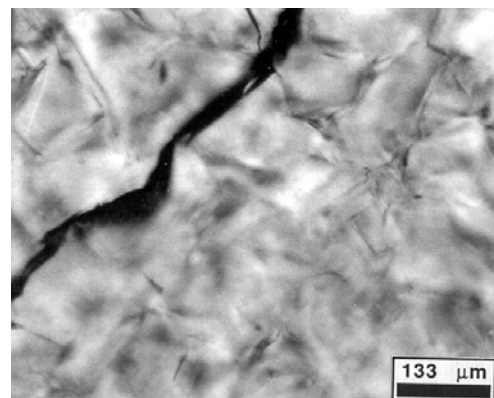
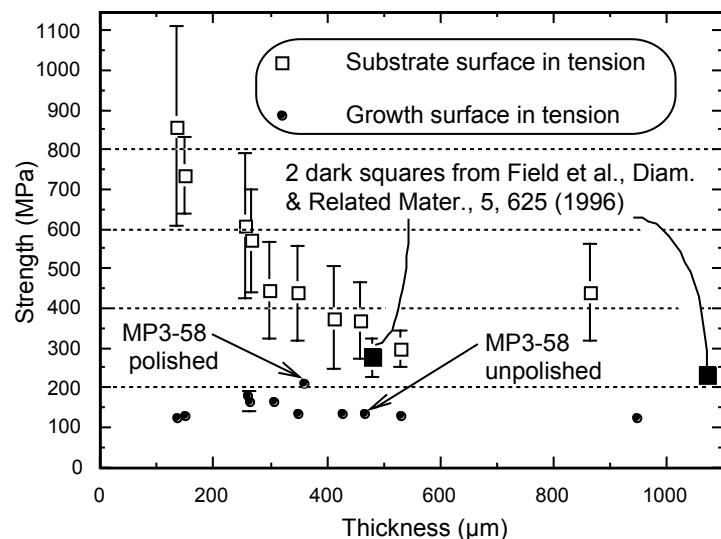


Figure 14. Comparison of infrared transmission of Norton CVD diamond with Type IIa natural diamond showing improvement in CVD diamond between 1990 and 1993.

Thermal shock resistance was excellent, but limited by the relatively low mechanical strength of CVD diamond. Under most diamond growth conditions, a very fine grain material nucleates on the substrate (which is typically molybdenum) and grains grow in a conical shape as the deposit gets thicker. By the time a millimeter of diamond has been deposited, the grains on the upper (growth) surface can be $>100\ \mu\text{m}$ in diameter, while grains on the lower (substrate) surface remain $<1\ \mu\text{m}$. Grains are laced with microscopic defects and cracks (Figure 15) and can be highly stressed. Grain boundaries are enriched in non-diamond carbon and can exhibit mechanical weakness. The mechanical strength of ceramic materials tends to decrease as grain size increases, because the flaws between large grains are potentially larger in dimension than the flaws between small grains.

Figure 15 shows the mechanical strength of Raytheon CVD diamond tested in biaxial flexure.¹⁹ The strength when the coarse-grain side is in tension is about half the strength observed when the fine-grain side is in tension. For Raytheon material, the strength of the coarse-grain side is independent of the thickness of the growth, whereas the strength of the fine-grain side decreases with increasing diamond thickness. By contrast, both surfaces of DeBeers CVD diamond become weaker as thickness increases from 0.5 to 2.5 mm.²⁰ However, Table 2 shows that the fine-grain surface of DeBeers material is twice as strong as the fine-grain surface of Raytheon material, even though the DeBeers material was tested in an unpolished state. The coarse-grain surfaces do not differ by nearly as much. DeBeers reports that the Weibull modulus of its material is in the range 10–20, which means that there is little variation in strength from sample to sample. A high Weibull modulus is desirable for reliability of a mechanical design. Despite attempts to alter the microstructure and growth chemistry, the mechanical strength of Raytheon CVD diamond has not changed significantly from the time it was first measure in 1992 until the latest measurements in 2000.



Defect observed 0.57 mm below surface of polished CVD diamond

Figure 15. *Left:* Biaxial flexure strength of Raytheon CVD diamond coarse-grain growth surface is low and appears to be independent of diamond thickness. Strength of fine-grain substrate surface is high, but decreases as the thickness of the diamond increases. *Right:* Example of flaw that might be non-diamond carbon or a crack running along grain boundaries deep inside a polished specimen of Raytheon CVD diamond.

Table 2
Comparison of 3-Point Flexure Strength (MPa) of Optical Diamond from Raytheon and DeBeers*

Surface in tension	Raytheon [†]	DeBeers [‡]
Fine-grain (substrate surface)	478 ± 52 (6 bars)	~880
Coarse-grain (growth surface)	317 ± 15 (6 bars)	~400

*Rectangular bars 18 × 2 mm × 1.0 to 1.2 mm thick. Outer support separation = 15 mm

[†]Polished surfaces. Samples measured in 2000.

[‡]Unpolished surfaces. Samples from 1997.¹⁹

To verify that the thermal shock resistance of diamond was indeed very great, thin windows from the early 1990s were subjected to a Mach 5 sled test side-by-side with two sapphire windows in 1998. A 0.7-mm-thick × 19-mm-diameter diamond disk (Figure 16) subjected to a heat flux of 320 W/cm² survived a test in which two sapphire disks (2 mm thick × 25 mm diameter) fractured.

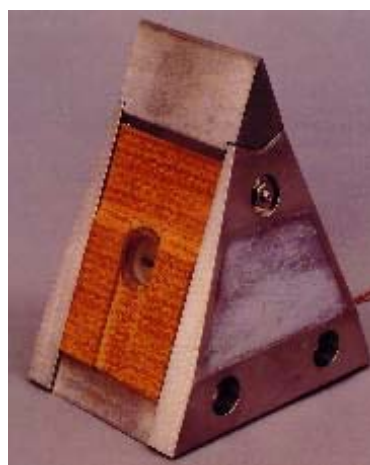


Figure 16.
Diamond disk mounted on wedge for Mach 5 sled test.

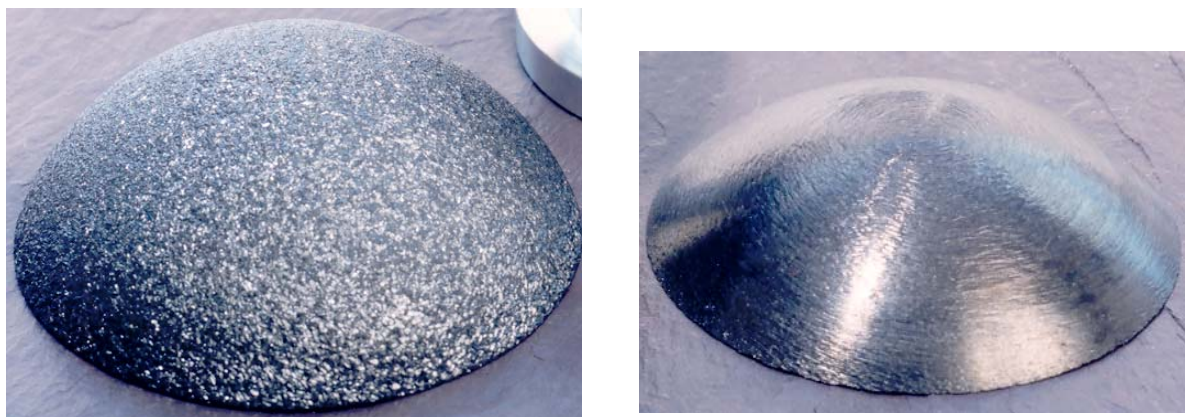


Figure 17. *Left:* As-grown CVD diamond dome from Raytheon with an outer surface roughness of $\sim 100\ \mu\text{m}$. The inside surface, which is not shown, is as smooth as the molybdenum mandrel on which the diamond was deposited. *Right:* Surface roughness reduced to $0.5\ \mu\text{m}$ after smoothing with a computer-controlled YAG laser.

DIAMOND DOMES AND LARGE WINDOWS

In the mid 1990s the focus of the Navy program shifted from learning to make good quality diamond on to making diamond domes. The goal was to produce polished, antireflection-coated, optical-quality diamond with a diameter of 60 mm and a thickness of 1.5 mm. By this time the contract effort had narrowed down to just Raytheon, which appeared to have the best success in making large, high quality diamond. A contract during the 3-year period 1996-1998 failed to make a single polished dome despite tremendous effort.

Initial obstacles that were overcome were optimizing the microwave plasma for uniform deposition over a hemispheric shape, maintaining temperature uniformity in the mandrel, ensuring safe release of the diamond from the mandrel during cooldown, and maintaining constant, clean conditions for the many weeks required for a single growth run. Several full-thickness dome blanks were grown and an automated method was developed to use a YAG laser to smooth the rough outside of the dome to the shape of a hemisphere (Figure 17).

The insurmountable obstacle proved to be polishing. Normally, materials are ground and polished by using abrasives that are harder than the work piece. There is no material harder than diamond, so abrasive grinding of diamond with industrial diamond powder is a very inefficient process. Many methods of shaping CVD diamond were explored in the early and mid 1990s, including such approaches as ion etching or dissolving diamond in hot iron or hot lanthanide metals. In fact, when the Navy program was making significant progress in growing high quality diamond, funding was diverted from the diamond deposition program into parallel contracts to explore methods of shaping diamond. Contracts were issued in 1994 to Rocketdyne for shaping with an ultraviolet laser and to Auburn University for dissolving diamond with hot iron. Neither contract made good progress and funding was discontinued after just one year. Earlier, Raytheon had experimented with hot metal dissolution of diamond, but never found a good way to precisely control the shaping process to obtain the necessary optical figure.

Raytheon struggled mightily to polish a diamond dome with diamond abrasive. The closest approach to success was a dome that was polished on most of its inner surface by diamond abrasive (Figure 18). However, some cracks developed and the dome fractured during the attempt to polish the outer surface.

DeBeers received a contract from the British Defence Evaluation and Research Agency to produce polished diamond domes and did succeed in 1999 (Figure 19).²¹ DeBeers apparently has proprietary methods to polish diamond more than an order of magnitude more efficiently than methods used at Raytheon.



Figure 18. *Left:* Diamond dome polished on the inside surface at Raytheon in 1997. The outer annulus is still rough and was never fully polished. A reflection of the photographer can be seen at the left side. The metal spindle is glued to the diamond to hold it for polishing the outside surface. *Right:* Fully polished diamond dome displayed in public by DeBeers in 1999.

After deciding that U.S. technology was not advanced enough to produce polished diamond domes, a final goal was set for another contract at Raytheon beginning in 1999. The products of this successful work were three almost rectangular windows with dimensions of 125×25 mm and a thickness near 1.3 mm (Figure 20).

DIAMOND TODAY

During the 1990s many laboratories around the world mastered the art and science of depositing high quality CVD diamond. Although there were numerous commercial ventures to produce diamond—and wild predictions of vast markets that lay ahead—only DeBeers remains a commercial supplier of optical quality CVD diamond in 2002. Raytheon has the capability of producing the material, but presently lacks outside customers.

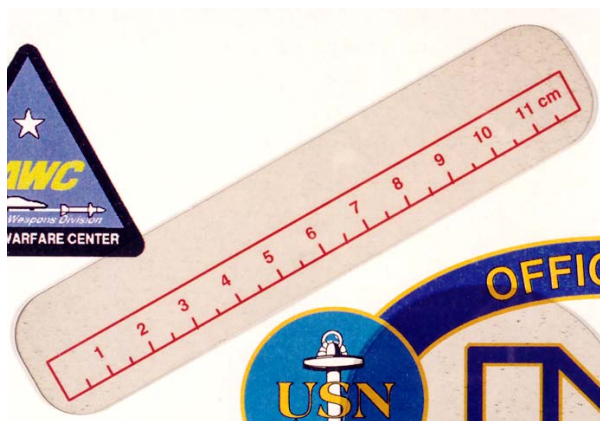


Figure 19. Fully polished, flat CVD diamond window (1.3 mm thick) produced by Raytheon in 2000.

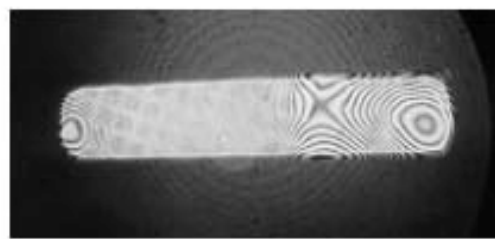
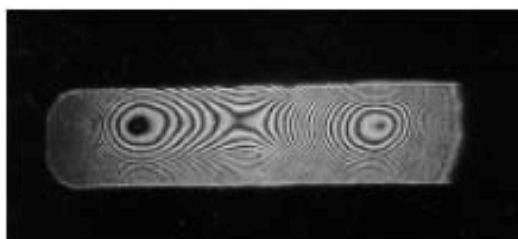


Figure 20. Interferometric measurement of flatness of two sides of polished diamond window, such as the one in Figure 19. Each contour line in the interferogram represents $\sim 0.3 \mu\text{m}$ vertical relief from the neighboring contour.

Commercial CVD diamond products from DeBeers in 2001 are listed in Table 3. Diamond has special advantages in applications requiring high thermal conductivity. For example, the newest high-power industrial CO_2 lasers are so powerful that they create thermal gradients in the ZnSe laser window. The temperature gradient gives rise to a refractive index gradient which distorts the beam of light emerging from the laser. Diamond has such a high thermal conductivity that the gradients are smaller and the beam distortion is significantly less. For megawatt-power microwave tubes, an edge-cooled diamond window is essentially the only suitable material. Other potential windows cannot be adequately cooled to survive the high power levels.

It remains to be seen whether the fledgling commercial market for CVD diamond will be strong enough to eventually reduce the price of the material and keep diamond available for future military applications as sensor windows and microwave windows.

Table 3
Commercial Markets for DeBeers CVD Diamond in 2001

• Optical-Quality CVD Diamond • CO₂ laser windows: diamond replaces zinc selenide 33 × 12 × 0.7 mm rectangles Radial temperature gradient in diamond is 1/10 of gradient in ZnSe Flatness of <2 HeNe fringes in 1-inch area • Radio-Frequency CVD Diamond • 1-megawatt gyrotron tubes for nuclear fusion research Water cooled edges keep aperture cool 106 mm diameter × 1.8 mm thick Loss tangent = 3×10^{-5} at 144 GHz Can withstand 7 bar pressure and 450°C • Thermal Management CVD Diamond (largest market today) • High-power In-Ga-As laser diodes and diode arrays 100 W output / 200 W electrical input Array mounted on diamond plate (11 × 3 × 0.3 mm) Diamond transports heat from diode to heat sink For every 11°C lowering of the diode junction temperature, lifetime doubles 3 diamond grades from DeBeers: conductivity = 1000, 1500, or 1800 W/m·K Grown in 158-mm-diameter disks Ground to flatness of 1 μm per millimeter over a 10 mm span • Precision Cutting Tools • Surgical knives for histology and ophthalmic surgery Fine grain black material (0.2-0.5 mm thick)

ACKNOWLEDGEMENT

Most of the work described in this paper was supported by the Office of Naval Research.

REFERENCES

- ¹ M. Seal and W. J. P. van Enckevort, "Applications of Diamond in Optics," *Proc. SPIE* **1988**, 969, 144.
- ² R. W. Boese, J. B. Pollack, and P. M. Silvaggio, "First Results from the Large Probe Infrared Radiometer Experiment," *Science* **1979**, 203, 797.
- ³ R. M. Hazen, *The Diamond Makers*, Cambridge University Press, Cambridge, 1999.
- ⁴ W. G. Eversole, "Synthesis of Diamond," U.S. Patent 3,030,187 (17 April 1962).
- ⁵ B. V. Derjaguin and D. B. Fedoseev, "Synthesis of Diamond at Low Pressure," *Scientific American*, November 1972, p. 102.
- ⁶ J. C. Angus, H. A. Will, and W. S. Stanko, "Growth of Diamond Seed Crystals by Vapor Deposition," *J. Appl. Phys.* **1968**, 39, 2915.

- ⁷ S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, "Vapor Deposition of Diamond Particles from Methane," *Jap. J. Appl. Phys.* **1982**, 21, L183.
- ⁸ Y. Saito, S. Matsuda, and S. Nogita, "Synthesis of Diamond by Decomposition of Methane in Microwave Plasma," *J. Mater. Sci. Lett.* **1986**, 5, 565.
- ⁹ T. R. Anthony and J. F. Fleischer, "Transparent Diamond Films and Method for Making," U.S. Patent 5,110,579 (5 May 1992); T. R. Anthony and J. F. Fleischer, "Substantially Transparent Free Standing Diamond Films," U.S. Patent 5,273,731 (28 December 1993).
- ¹⁰ S. J. Harris and D. G. Goodwin, "Growth on the Reconstructed Diamond (100) Surface," *J. Phys. Chem.* **1993**, 97, 23.
- ¹¹ W. D. Partlow, R. E. Witkowski, and J. P. McHugh, "CVD Diamond Coatings for the Infrared by Optical Brazing," in *Applications of Diamond Films and Related Materials* (Y. Tzeng, M. Yoshikawa, M. Murakawa and A. Feldman, eds.), Elsevier, Amsterdam (1991), p 163.
- ¹² R. H. Hopkins, W. E. Kramer, G. B. Brandt, J. S. Schruben, R. A. Hoffman, K. B. Steinbruegge, and T. L. Peterson "Fabrication and Evaluation of Erosion-Resistant Multispectral Optical Windows," *J. Appl. Phys.* **1978**, 49, 3133.
- ¹³ R. J. Ondercin, L. M. Goldman, and A. B. Harker, "Development of a Repairable IR Composite Window," *Proc. SPIE* **1999**, 3705, 238.
- ¹⁴ R. Gentilman, "Preventing Rain Erosion Damage to ZnS and ZnSe Window with a Compliant Intelayer," *Proc. 5th DoD Electromagnetic Windows Symposium*, Boulder, Colorado, October 1993, p. 203.
- ¹⁵ A. B. Harker and J. F. DeNatale, "Diamond Gradient Index 'Moth-Eye' Antireflection Surfaces for LWIR Windows," *Proc. SPIE* **1992**, 1760, 261.
- ¹⁶ J. M. Trombetta, J. T. Hoggins, P. Klocek, and T. A. McKenna, "Optical Properties of DC Arc-Discharge Plasma CVD Diamond," *Proc. SPIE* **1991**, 1534, 77.
- ¹⁷ T. McKenna, J. T. Hoggins, J. M. Trombetta, and P. Klocek, "Optical-Quality, High-Growth-Rate, Arc-Jet CVD Diamond," *Proc. SPIE* **1994**, 2286, 160.
- ¹⁸ D. C. Harris, *Development of Chemical-Vapor-Deposited Diamond for Infrared Optical Applications. Status Report and Summary of Properties*, TP 8210, Naval Air Warfare Center, China Lake, July 1994.
- ¹⁹ C. B. Willingham, T. M. Hartnett, R. P. Miller, and R. B. Hallock, "Bulk Diamond for IR/RF Windows and Domes," *Proc. SPIE* **1997**, 3060, 160.
- ²⁰ J. A. Savage, C. J. H. Wort, C. S. J. Pickles, R. S. Sussmann, C. G. Sweeney, M. R. McClymont, J. R. Brandon, C. N. Dodge, and A. C. Beale, *Proc. SPIE* **1997**, 3060, 144.
- ²¹ C. J. H. Wort, C. S. J. Pickles, A. C. Beale, C. G. Sweeney, M. R. McClymont, R. J. Saunders, R. S. Sussmann, and K. L. Lewis, "Recent Advances in the Quality of CVD Diamond Optical Components," *Proc. SPIE*, **1999**, 3705, 119.