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Investigation of Applications of Diamond Film

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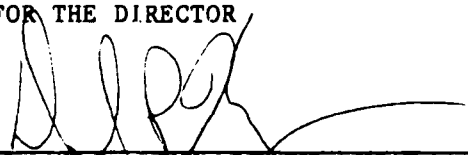
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The unique properties of synthetic diamond prepared by chemical vapor deposition suggest potential aerospace applications of interest to the Air Force. The status of the rapidly developing technology of low-pressure diamond film synthesis has been determined by contacts with 76 research groups active in the field. Information on six synthetic techniques and a list of 112 active groups are included. Updated diamond film properties are presented based on the survey, literature data, and the measurements made in this program. Measurements were made of hydrogen diffusion resistance, hardness, thermal shock resistance, rupture strength, and propellant compatibility.				
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19. Abstract (cont.)

A comprehensive screen of 200 potential Air Force applications is presented. These were reduced to 4 high-value applications: bearing surfaces, barriers for hydrogen diffusion, barriers for propellant corrosion protection, and thermal protection for surfaces with localized high heat flux. Initial reports of unusually high tensile strength for diamond films cannot be supported by detailed analysis of test data, eliminating some structural applications. Technology development plans are presented for obtaining better properties data and for demonstrating the application of diamond films to bearings.

ACKNOWLEDGEMENTS

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1.0 EXECUTIVE SUMMARY

The impressive physical properties of diamond and the recently developing capability for its low-cost synthesis have opened up the potential for the use of diamond as an engineering material. Diamond is the hardest material known; it has a room temperature thermal conductivity five times that of copper, a coefficient of friction equal to that of Teflon, is resistant to oxidation, and chemically inert to most reactive materials to moderately high temperatures. It has good physical properties: compressive strength of 16×10^6 psi, tensile strength of 0.5×10^6 psi, and a Young's modulus of 150×10^6 psi. In addition, it has unique optical and electrical properties.

Within the last decade, researchers have been actively developing a variety of techniques for deposition of diamond using low-pressure, moderate-temperature chemical vapor deposition (CVD) processes in the form of thin films on various substrates. Within the last few years, synthetic diamond films have been commercially applied.

Because of the significant potential for use of diamond in high-performance aerospace applications, the Astronautics Laboratory (AFSC) conducted this program to investigate synthetic diamond. This six-month technical effort had as its objectives:

- . Identification of applications for diamond within the astronautics and propulsion industries.
- . Determination of key properties needed to confirm the applications.
- . Identification of the critical paths necessary to develop the applications.

The four-phase program, begun in September 1988, consisted of:

Phase I - Survey of Diamond Film Technology

To determine the state-of-the-art, questionnaires were sent to 76 of the 112 groups identified as active in diamond film synthesis. The 23 responses received give a current picture of the capabilities and directions of this rapidly expanding field.

Using the survey results, projections of production capability have been made, and, along with reviews of the recent literature, an updated table of diamond film properties has been prepared.

Phase II - Applications Concept Development

The substantial superiority of diamond's properties over those of presently used engineering materials suggests that many aerospace applications should be attractive. A

matrix of 26 of the properties by the 200 applications they enhance was prepared and screened to isolate applications of high value to the Air Force.

The high-value applications identified initially were:

- . Bearing surface coating
- . Composite structural material
- . Hydrogen diffusion barrier
- . Monolithic structural material
- . Thermal protective coating

Phase III - Preliminary Characterization

Properties critical to the high-value applications were identified and measurements of four were made by the contractor. One other was measured by AL using diamond film specimens supplied by the contractor.

The properties measured were:

Hydrogen Diffusion--Determined to be less than the limits of detection for a 0.5 micron (0.02 mil) thick film (limit of detection = 6×10^{-10} std $\text{cm}^3 \text{sec}^{-1}$), indicating that diffusion barrier applications should be considered.

Microhardness--For films on a strong substrate (molybdenum) the hardness is at the limits of measurement = $10,000 \text{ Kg mm}^{-2}$, which equals natural diamond, indicating bearing applications should be considered.

Thermal Shock Resistance--Diamond deposited on molybdenum withstands at least 100 cycles from ambient to liquid nitrogen temperature without degradation, indicating it may be practical for coatings in cryogenic applications.

Rupture (Tensile Strength) Tests--Results of these tests are ambiguous. Detailed analysis indicates a tensile strength of about 500,000 psi, similar to that of natural diamond. Although this is an impressive value, especially considering the relative lack of process maturity, and is adequate for many applications, it does rule out for present consideration some structural applications, such as monolithic pressure vessels, and makes other applications, such as composite structures, less attractive.

Propellant Compatibility--(Astronautics Laboratory (AFSC) measurement) Exposure tests of free-standing 40-micron diamond film to ClF_3 and N_2O_4 vapor, and N_2H_4 liquid showed no reaction.

Phase IV - Applications assessment and Development Planning

Diamond film bearing applications were examined and a program to demonstrate this technology was outlined. It is recommended that this program be preceded by a one-year effort to quantify more diamond film properties in conjunction with process development to assure optimization and control of properties.

Conclusions and Recommendations

Synthetic CVD diamond is a high-value material with significant engineering applications and a potential for relatively low cost. Its properties should be further documented and optimized and the technology for its application to turbopump bearings should be demonstrated.

2.0 PROGRAM DESCRIPTION

This program was conducted by the Astronautics Laboratory (AFSC) to identify potential high-value applications of diamond film to its aerospace missions. To do this required determination of the state-of-the-art of diamond film technology, both to identify realistic synthesis capability and its properties. Natural diamond has some attractive engineering properties which have not been exploited because of the limited availability and form of the material. The evolution of CVD diamond synthesis provides the capability to produce synthetic diamond economically in geometries useful for engineering applications.

Along with the state-of-the-art data, a wide range of Air Force applications were identified which would be benefitted by the known or potential superiority of the properties of CVD diamond over conventional materials. Since some properties were uncertain, their experimental determination was undertaken to provide preliminary values on which to base further study of selected applications. Measurements were made of hardness, hydrogen diffusion resistance, thermal cycle adherence, rupture strength, and propellant corrosion compatibility.

The 200 potential applications identified were screened to five high-value applications: bearings, composite structures, hydrogen diffusion barriers, pressure vessels, and thermal protection coating. After further study of these applications and assessment of the new properties data, the bearing application was chosen as the best suited for near-term technology demonstration. A recommended program is outlined for proving the technological feasibility of diamond film for bearing applications.

Since many engineering properties of diamond film have not been measured, it is recommended that the initial study be concentrated on basic properties measurement of CVD diamond.

The Investigation of Applications of Diamond Film program consisted of four phases, which included:

- | | | |
|-----------|---|--|
| Phase I | - | Survey of Diamond Film Technology |
| Phase II | - | Applications Concept Development |
| Phase III | - | Preliminary Characterization |
| Phase IV | - | Applications Assessment and Developmental Planning |

These phases are outlined below and described in the following sections.

2.1 PHASE I - SURVEY OF DIAMOND FILM TECHNOLOGY

The purpose of this phase was to determine the capability for diamond film synthesis and the extent of developmental activity in the field. Many research groups

were identified and asked to provide data on their synthesis techniques and diamond deposition capability. The data from this survey are discussed in Section 3.1.

An updated listing of diamond properties was prepared based on these contacts and the literature. Information on eight different synthesis processes was obtained in the survey. Projections of process capability and production cost estimates were prepared for these processes.

Five sources of extensive data on diamond film synthesis were identified and are discussed in Section 3.4.

2.2 PHASE II - APPLICATION CONCEPT DEVELOPMENT

A matrix of possible applications of diamond film in the aerospace field and the significant properties of diamond film which promote the applications was prepared and is presented in Section 4.

By considering various measures of value to the Air Force of these applications, they were screened to a small number of potentially high-value uses for further consideration.

2.3 PHASE III - PRELIMINARY CHARACTERIZATION

In the process of application development, critical properties of diamond film were identified, which are needed to assess the potential value of the application. Five of these properties, hydrogen diffusion rate, hardness, thermal cycling adhesion, rupture strength, and propellant corrosion resistance were measured on this program. This testing and its results are described in Section 5.

2.4 PHASE IV - APPLICATIONS ASSESSMENT AND DEVELOPMENTAL PLANNING

In this phase, a high-value propulsion application of diamond films, surfaces for bearing elements in turbopump systems, was assessed. A plan for a program to demonstrate the technology for diamond-film bearings was prepared. Because of the large amount of basic properties data which still must be defined for CVD diamond film, a recommendation has been made to precede the technology development with extensive laboratory characterization studies. These planned activities are described in Section 6.

2.5 CONCLUSIONS

The conclusions of the present study are:

(1) A broad base of academic and industrial researchers is active in development of diamond film synthesis.

(2) A number of synthetic approaches is under development, with no clear leader at the present time.

(3) The properties of CVD diamond film generally appear to match those of natural diamond.

(4) Initial applications being developed utilize small quantities of diamond film in very high-value uses in terms of \$/Kg. However, there is no fundamental barrier to high-volume applications of diamond film as an engineering material, since it uses readily available, inexpensive, nonstrategic synthesis materials with little or no environmental problems.

(5) Lack of well-characterized properties and of demonstrated pilot applications limit the use of diamond film in engineering applications.

3.0 STATUS OF DIAMOND FILM TECHNOLOGY

The state-of-the-art of diamond film technology status is defined by:

- (1) Those groups active in the field.
- (2) The current development status of synthesis capabilities.
- (3) The engineering properties which can be obtained with CVD diamond, as contrasted with those of the natural material.

As might be expected for what appears to be an exploding technology area, several groups are active in defining the CVD diamond field from a range of viewpoints.

3.1 ACTIVE RESEARCH GROUPS

During initial consideration of the subject, it was assumed that contact with perhaps two dozen research groups would cover the field. In fact, over 150 individuals in 112 groups were identified. These are listed in Table 1, which is by no means all-inclusive of those working on CVD diamond synthesis.

Although the history of CVD diamond synthesis will not be covered here, it can be generalized as beginning with early Soviet and American work in the mid-50s, followed by Japanese and American studies in the late 70s (Table 2, based on Ref. 1). Most extensive work has been concentrated in Japan, as indicated by the patent history shown in Table 3 from Ref. 2 and the relative R&D investment shown in Figure 1.

To obtain data on technology status, a standardized survey was prepared and sent to 82 of the groups believed to be active in some aspect of CVD diamond synthesis. Because of the importance of the Japanese work, a cross-section of 10 groups was contacted through the efforts of Mitsui & Company, Ltd., which volunteered its services and allowed us to overcome the language barrier.

The survey process consisted of an initial telephone contact, followed by transmittal of a copy of the survey with a descriptive cover letter (Figures 2 and 3). Responses were received from the 23 groups listed in Table 4. It is likely that some groups believed that it was not in their best interest to respond to the survey although, in follow-up calls, this attitude was expressed by only one individual.

Respondents were cautioned not to include proprietary data in their responses, which further limited the data provided. Because of this factor and the selective responses, the survey cannot be considered to be a statistically exact definition of the field. It does provide a snapshot of the status of a significant number of research groups and their approaches to diamond synthesis.

TABLE 1. Groups Active in Diamond Film Synthesis, Page 1 of 2

INSTITUTION	COUNTRY	NAME	PHONE NO.	ADDRESS
	Austria	Lux, B.		
	FRG	Kosdl, P.		
	USSR	Fedoseev, D. B.		
	USSR	Dervacin, B. V.		
3M Company	US	Yu, Edward C.	617-733-1110	3M Center, 219-15-01, St. Paul, MN 55119
Advanced Fuel Research, Inc.	US	Morrison, Philip W., Jr.	203-528-9806	87 Church Street, East Hartford, CT 06108
Advanced Tech Materials, Inc.	US	Beetz, Charles	203-333-2681	520-9 Danbury Rd.
Air Force, Wright-Patterson AFB	US	Haas, Dr. T. W.	513-255-5892	AFWAL/MLBN, Wright-Patterson AFB, OH 45433
Air Force Office of Scientific Research	US	Schioler, Dr. Lise'	202-767-4933	AFOSR/NE, Bolling AFB, DC 20332-6600
Air Products and Chemicals	US	Hoover, Dr. David S.	215-481-4772	
Akad. Nauk Ukrain. SSR	USSR	Maidich, Iu. V.		Kiev, Ukra. SSR
AMP Inc.	US	Deeg, Dr. Emil W.	717-986-5118	
Aoyama Gakuin Univ.	Japan	Inuzuka, T.		Tokyo, Japan
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Armstrong World Industries	US	Wiansosky, Dr. Jerome	717-396-5288	
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AT&T Bell Laboratories	US	Hucha, John A.	201-582-3000	600 Mountain Avenue, Murray Hill, NJ 07974
Auburn University	US	Davidson, Dr. James L.	205-887-1873	200 Broun Hall, Auburn Univ., Ala., 36849
Babcock & Wilcox Contract Research Div.	US	Clevinger, Gary S.	703-385-2000	P.O. Box 10935, Lynchburg, VA 24506
Barr & Stroud, Ltd.	UK	Orr, J. S.		Glasgow, Scotland
Bausch & Lomb	US	Cumho, M. J.	716-338-5960	
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General Electric R&D Center	US	De Vries, Robert	516-399-5225	17 Van Vorst Dr., Burnt Hills, NY 12027
STE Laboratories	US	Oblas, Dr. Jan	617-466-2456	
Guelph Univ.	Canada	Macdonald, J. R.		Canada
Gulf & Western Applied Sci. Labs.	US	Aisenberg, S.		333 Bear Hill Road, Waltham, Mass 02154
Hercules, Inc.	US	Ho, Dr. Floyd F.-L.	302-995 3321	
Honeywell Corp. Tech. Center	US	Moravec, T. J.		10701 Lyndale Ave., S, Bloomington MN 55420
Honeywell Systems & Research	US	Lee, James C.	612-876-5200	3660 Technology Drive, P.O. Box 1361, Minneapolis MN 55440
Hughes Aircraft Co.	US	Gardos, Michael N.	213-616-9890	P.O. Box 902, El/F150, El Segundo, CA 90245
IBM Almaden Research Center	US	Schi, Dr. Haj	408-927-1080	K33/802, 450 Harry Road, San Jose, CA 95120
IBM Yorktown Hts. Lab.	US	Cusano, Jerome	914-945-1357	Manager, CCS Materials Lab., IBM, Thomas J. Watson Research Center, PO Box 218, Yorktown Heights, NY 10598
Idemitsu Petrochemical Co., Ltd.	Japan	Ito, Kazuomi	03-546-6690	4-12-18 Binza, Chuokku, Tokyo, Japan
Institute of Physical Chem., Moscow	USSR	Spitsyn, Boris B.		Moscow, USSR
IDLAB Corp.	US	Savano, Dr. R. Ray	714-399-1353	
Ionic Atlanta, Inc	US	Logg, Keith O.		Atlanta, GA
Kanagaki	Japan			
Kennametal, Inc.	US	Bauer, Eric S.	412-638-2037	
Lincoln Labs., MIT	US	Seis, Michael	617-981-4658	MIT Lincoln Labs., 244 Wood St., Mail Stop I 3006, Lexington, Mass., 02173
Los Alamos Nat. Lab	US	Reenan, Brian		Los Alamos, NM
Martin Marietta Labs	US	Venables, John D.	301-247-0700	Associate Director, Martin M. Labs., 1450 South Rolling Rd., Baltimore, MD 21227
Martin Marietta Orlando	US	Li, Dr. Tom P.L.	407-356-2914	
McDonnell-Douglas Research Labs.	US	Limnfield, Harvey V.	314-232-0232	814q. 110, Box 516, St. Louis, MO 63166
Microscience, Inc.	US	Popov, Dr. Oleg	617-871-0308	41 Accord Park Drive, Norwell, MA 02061
Mitsubishi Metal Corp.	Japan	Osawa, Y.		
NASA, OAGT	US	Fusaro, Dr. Robert		Code RM, NASA Headquarters, Washington, D.C. 20546
NASA LeRC	US	Smec, Diane H.	216-433-2309	NASA Lewis Research Center, Electro-Physics Branch, 21000 Brookpark Rd., N.S. 302-1, Cleveland, OH 44133

TABLE 1. Groups Active in Diamond Film Synthesis, Page 2 of 2

National Institute of Standards and Tech.	US	Feldman, Albert	301-975-5740	Group Leader, Optical Materials Group, National Bureau of Standards, A257 Materials Building, Gaithersburg, MD 20899
National Materials Advisory Board, NRC	US	Lane, Dr. Joseph R.	202-334-3303	Senior Program Officer, (NMAB), National Research Council, 2101 Constitution Ave., Washington, D.C. 20418
Nat. Aerospace Lab.	Japan			
Nat. Inst. Res. Inorganic Matls.	Japan	Kobayashi, Toyohiko		Sakura, Japan
Nat. Space Dev. Agency	Japan			
Naval Research Labs.	US	Butler, Dr. James E.	202-767-1115	Mail Code 6174, NRL, Washington, DC 20375
Naval Weapons Center	US	Schwartz, Dr. Robert		Code 373, Naval Weapons Center, China Lake, CA 93555
Nebraska Univ.	US	Bu-Abbud, S.		Lincoln, Neb
North American Phillips Corp.	US			
North Carolina State Univ.	US	Glass, Jeffry		
Norton Co.	US	Dr. Bell, Peter M.	508-795-5000	VP, Corp Tech., One New Bond ST., Worcester, MA 01606-2698
Norton Co., Norton Christensen, Inc.	US	Bigelow, Dr. L. K.	901-972-3140	2532 South 3270 west, Salt Lake City, UT 84119
OCLI Corp	US	Gurev, M.		2789 Northpoint Parkway, Santa Rosa, CA
Office of Naval Research	US	Yoder, Max	703-696-4218	Code 1114Y, 900 N. Quincy St., Arlington, VA 22217-5000
Office of Naval Technology	US	Kinna, Marlin	202-696-4791	Chairman, Joint Directors of Laboratory Tech. Panel, 800 N. Quincy St., Arlington, VA 22217
Old Dominion Univ.	US	Albin, S.		Norfolk, VA
Optical Coating Lab, Inc.	US	Apfel, Joseph H.	707-545-6440	2789 Northpoint Parkway, MS 121-1, Santa Rosa, CA 95407
Osaka Diamond Ind. Co.	Japan	Tomisori, H.	0722-62-1061	80 Ohtorikita-Machizono, Sakai-shi, Osaka, Japan
Osaka Univ.	Japan	Suzuki, Jun-ichi		Suita, Japan
Penn. State Univ.	US	Roy, Rustum	814-865-3704	265 Materials Research Laboratory, University Park, PA 16802
Perkin-Elmer Corp., Metco Div.	US	Reardon, Joseph D.	516-334-1300	1101 Prospect Ave., Westbury, NY 11590
Phillips Laboratories	US	Bloom, Gerald	914-945-6000	345 Scarborough Road, Briarcliff Manor, NY 10510
Phillips & DuPont Optical Co.	US	Johnson, Dr. George H.	302-999-4814	
PPS Industries, Inc.	US	Welch, Dr. Cletus W.	216-848-4161	
Raytheon Company	US	Tustison, Dr. Randall W.	617-860-3030	
Research Triangle Inst.	US	Rudder, R. A.		
Rocketdyne, Inc.	US	Holly, Dr. Sander	818-700-4839	
Royal Signals and Radar Establish.	UK	Lettington, A. H.		Malvern, England
Scientific Research Associates, Inc.	US	Brubin, Harold L.	203-659-0333	50 Mye Road, Glastonbury, CT 06033
Showa Denko K.K.	Japan	Komaki, Kunio	03-733-0151	2-24-25 Tanagawa, Ohta-ku, Tokyo, 146 Japan
Spectran Corp	US			
Stratabit, Inc.	US	Dennis, Dr. Mahlon O.	713-999-4530	
Suaitono Electric Industries, Ltd.	Japan	Nishimura, A	03-423-5207	3-12, Motoakasaka, 1-Chome, Minato-ku, Tokyo, 107 Japan
Texas Instruments	US	Purdes, Andrew J.	214-995-5559	MS 147 P.O. Box 655936, Dallas, TX 75265
Toaki Univ.	Japan	Iida, Masamori		Hiratsuka, Japan
Tokyo Univ. of Agr. & Tech.	Japan	Komatsu, K.		
Toshiba Corp.	Japan	Sawabe, Atsunobu	044-549-2116	1 Komukai Toshiba-cho Saiwai, Kawasaki 210 Japan
Tottori University	Japan	Nishimori, K.	0857-28-0321	101, Minami 4-Chome, Koyama-cho, Tottori City, Japan
Toyota	Japan			
United Technology Research Center	US	Roman, Ward C.	203-728-7000	Silver Lane, MS 90, East Hartford, CT 06108
Universal Energy Co.	US	Moo, Dr. Richard		
University of Texas	US	Collins, Carl B.	214-690-2111	2601 Floyd Road, Richardson, TX 75083
Univ. of Colorado	US	Cash, Webster C.		Boulder, CO
UTI Corp.	US	Harrois, Dr. Nicholas	215-539-0700	
Varian Research Center	US	Reynolds, Glyn	415-493-4000	511 Hansen Way, N/S K-105, Palo Alto, CA 94303
Wavemet, Inc.	US			
Wayne State University	US	Pryor, Roger W.	313-577-0846	666 West Hancock Street, Detroit, Mich 48202
Westinghouse	US	Constock, Robert	412-256-1277	Pittsburg, PA
Westinghouse Electric Corp.	US	Bewco, Dr. S.	301-765-4617	
Westinghouse R&D Center	US	Choyke, W. J.		Pittsburgh, PA 15235
W. J. Schafer Associates	US	Fleming, Dennis P.	703-558-7900	1901 North Ft. Myer Dr., Suite 800, Arlington, VA 22209
Terox Webster Research Center	US	Machonkin, M.A.	716-422-9411	800 Philips Road, Bldg. 114-41D, Webster, NY 14580

TABLE 2. Events in Early History of Gas Phase Diamond Synthesis

DATE	INDIVIDUAL	ORGANIZATION	ACCOMPLISHMENT
1956	B.V. Derjaguin and D.V. Fedoseev	Inst. Phys. Chem. Acad. Sci., USSR	Patent application for gas phase synthesis
1956	H. Schoellenmeier	Potsdam Teachers College, E. Germany	Diamond films from acetylene in electrical discharge
1956	H. G. Eversole	Union Carbide	Low pressure synthesis of diamond reported
1963	H. G. Eversole	Union Carbide	Issued patent on low pressure synthesis
1966	J.C. Angus	Case Western Univ.	Use of hydrogen to inhibit graphite formation
1977	L.L. Bouliov, B.V. Derjaguin, and B.V. Spitzyn	Inst. Phys. Chem. Acad. Sci., USSR	Diamond growth on nondiamond surfaces achieved
1979	E.C. Pickery	Diamond Squared Industries	Patent for single step process for diamond film synthesis
1980	B.V. Derjaguin and D.V. Fedoseev	Inst. Phys. Chem. Acad. Sci., USSR	Patent issued for gas phase synthesis
1982	M. Setaka, et al	Nat. Inst. Research in Inorg. Matls	Publication of Japanese research

TABLE 3. Patent Activity by Country

Diamond and Related Materials

	TOTAL	U.S.	JAPAN	OTHER
'63 - '77	58 100%	15 26%	3 5%	40 69%
1978	2	...	1	1
1979	4	...	...	4
1980	7	1	1	5
1981	10	6	2	2
1982	18	3	12	3
'78 - '82	41 100%	10 24%	16 39%	15 37%
1983	40	5	30	5
1984	89	5	71	13
1985	206	11	176	19
1986	167	4	150	13
1987	71	3	61	7
'83 - '87	573 100%	28 5%	488 85%	57 10%

Source: Penn State Diamond and Related Material Consortium Data Base

U.S versus Japan 1988

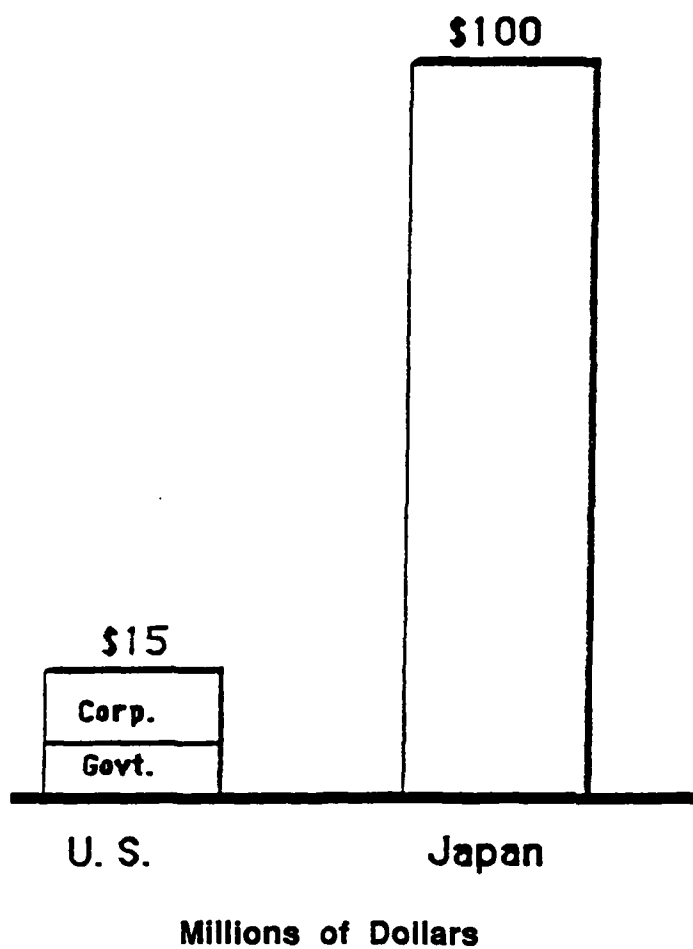


Figure 1. CVD diamond R&T investment.

DIAMOND FILM TECHNOLOGY SURVEY QUESTIONNAIRE

1. What are the names of those working on CVD diamond films at your facility?

2. How long has your organization been investigating CVD diamond films?

3. In general, what are the areas of CVD diamond film that you are investigating (i.e., deposition, properties, chemistry, etc.)?

4. What properties of CVD diamond films have you measured and what were the results?

5. What are your typical deposition parameters?

6. What do you use as precursors? Are you investigating other precursors? What are they?

7. How do you produce the atomic hydrogen? Are you investigating other methods? What are they?

Figure 2. Diamond film technology survey questionnaire, page 1 of 3.

Diamond Film Technology Survey Questionnaire (cont.)

8. What are typical deposition rates you obtain for CVD diamond films? What rates do you expect to be able to obtain in 2 years? In 5 years? In 10 years?

9. What methods do you use to characterize the CVD diamond films?

10. Are you investigating CVD diamond particles or other forms such as fibers?

11. Do you have any interest in growing diamonds or diamond film by other than low-pressure CVD or PVD?

12. What is the minimum deposition temperature you have used to deposit diamond (not DLC) films?

13. What applications of diamond film are you working on?

Are these: at concept stage? _____
 at development stage? _____
 or at production stage? _____

14. Please reference any recent reports or papers describing your work.

Figure 2. Diamond film technology survey questionnaire, page 2 of 3.

Diamond Film Technology Survey Questionnaire (cont.)

15. Please provide your comments on the status of diamond film technology, areas requiring work, and assessment of applications.

16. Please provide any descriptive or promotional literature on your organization's capabilities.

17. From your knowledge of the field, please provide names of other researchers who should be contacted for this survey.

- O -

You may / may not include my organization's name in the list of survey respondents.
(Circle One)

Survey Completed By: _____

Organization: _____

Please return to:

Bldg 2019-A2/Dept 9990
Aerojet TechSystems Company
P.O. Box 13222
Sacramento, CA 95813-6000

Figure 2. Diamond film technology survey questionnaire, page 3 of 3.

DRAFT

Date
Letter No.

Dr.
Title
Company
Address
City Zip

Dear Dr.,

As we discussed in our telephone conversation of DATE, I am surveying the status of diamond film technology. My interest is in its potential application to astronautics and propulsion. I am conducting this survey for the Air Force Astronautics Laboratory to help identify applications of interest to them, to assess the state of the art, and to identify critical paths necessary to develop the applications.

I realize that some information requested may be sensitive to your organization and expect you to limit your responses accordingly. Subject to Air Force approval, the results of the survey will be provided to the respondents. Capabilities will not be identified with your organization unless you specifically request this on the survey.

If you have information which you do not want to include in the survey, but which you wish to bring to the attention of the Air Force, this information can be so marked and will not be included in the published survey. If you prefer, you may contact the Air Force directly with the information. The Project Manager is Curtis C. Selph, AFAL/RKLC, Edwards AFB, CA 93523-5000. Mr. Selph's telephone number is 805-275-5168.

Your participation in this survey is appreciated. I believe the time spent will prove beneficial to increased applications for diamond films. Please feel free to contact me at 916-355-2849 if you have any questions. Thank you for your assistance.

Sincerely,

DMJ/rdw

Enclosures: (1) Diamond Film Technology Survey
(2) Return Address Label

Figure 3. Diamond film survey cover letter.

TABLE 4. Diamond Film Technology Survey Responses.

DIAMOND FILM TECHNOLOGY SURVEY RESPONSES

INSTITUTION	COUNTRY	NAME	PHONE NO.	ADDRESS
Air Force Office of Scientific Research	US	Schioler, Dr. Lise'	202-747-4933	AFOSR/NE, Bolling AFB, DC 20332-6600
Applied Science & Technology, Inc	US	Bourget, Larry	617-876-5545	40 Allston Street, Cambridge, Mass. 02139
Asahi Diamond Industries, Ltd.	Japan	Okuzumi, Fusimori	044-833-6221	185 Kuji Takatsu-ku, Kawasaki-shi, Kanagawa-ken, 213, Japan
Auburn University	US	Davidson, Dr. James L.	(205)887 1873	200 Brown Hall, Auburn Univ., Ala., 36849
BeamAlloy Corp.	US	Deutschman, Dr. Arnold H.	(614)766 3300	6360 Dublin Industrial Lane, Dublin OH 43017
Case Western Reserve Univ.	US	Angus, Prof. John C.	216-368-4133	Chem. Eng. Dept., Smith Building, Case West. Res. Univ., Case Institute of Tech, Cleveland, OH 44106
Crystallume	US	Pinneo, Michael	(415)-324-9681	125 Constitution Drive, Menlo Park, CA 94025
David Sarnoff Research Center	US	Seingh, Same	(609)734 2471	CM-5300 Princeton, NJ 08543
Diamond Materials Inst., Inc.	US	Orr, Ruznor	814-231-6200	2820 East College Ave., State College, PA, 16801
Fujitsu Laboratories, Ltd.	Japan	Kanarada, Dr. Motonobu	(0442) 48-3111	10-1, Wakahiya, Morinogato, Atsugi, Kanagawa Pref. Japan
Idemitsu Petrochemical Co., Ltd.	Japan	Ito, Kazuomi	03-544-6690	4-12-18 Siza, Chuo-ku, Tokyo, Japan
Mitsubishi Metal Co.	Japan	Tanaka, Yoshitaka	048-642-0511	1-297, Kitabukuro-cho, Ohmiya City, Saitama Pref., Japan
NASA Lewis Research Center	US	Smec, Diane M.	216-433-2309	NASA Lewis Research Center, Electro-Physics Branch, 21000 Brookpark Rd., N.S. 302-1, Cleveland, OH 44135
Naval Research Labs.	US	Butler, Dr. James E.	202-767-1115	Mail Code 6174, NRL, Washington, DC 20375
Naval Weapons Center	US	Schwartz, Dr. Robert		Code 373, Naval Weapons Center, China Lake, CA 93555
Morton Co., Norton Christensen, Inc.	US	Bigelow, Dr. L. X.	801-972-3140	2532 South 3270 west, Salt Lake City, UT 84119
Osaka Diamond Ind. Co.	Japan	Tominori, H.	0722-62-1061	80 Ohtorikita-Machizoho, Sakai-shi, Osaka, Japan
Shoma Denko K.K.	Japan	Kaseki, Kunio	03-733-0131	2-24-25 Yamagawa, Ohta-ku, Tokyo, 146 Japan
Sunited Electric Industries, Ltd.	Japan	Mishimura, A	03-423-5207	3-12, Motoakasaka, 1-Chome, Minato-ku, Tokyo, 107 Japan
Texas Instruments	US	Purdes, Andrew J.	(214)993 5359	MS 147 P.O. Box 659736, Dallas, TX 75265
Tokyo University of Agriculture	Japan	Koukita, Dr. A.	0423-81-4221	Koganei, Tokyo 184, Japan
Toshiba Corp.	Japan	Sanebe, Atsuhito	044-549-2116	1 Komukai Toshiba-cho Seimai, Kanagawa 210 Japan
Tottori University	Japan	Nishimori, K.	0857-28-0321	101, Minami 4-Chome, Koyama-cho, Tottori City, Japan
Wayne State University	US	Pryor, Roger W.	(313)577 0846	666 West Hancock Street, Detroit, Mich 48202

The raw survey responses, with names and other identifying data removed, are given in Appendix A. Data summaries from the responses are given below.

Question 1. "What are the names of those working on CVD diamond films at your facility?"

A total of 19 groups answered this question. The average group size was slightly over four people, with a range from 1 to 19. Typical group size was one to three people. The distribution of the data is shown in Figure 4. It is probable that, in some cases, the names listed do not include all personnel working on diamond film (e.g., support staff).

Question 2. "How long has your organization been investigating CVD diamond films?"

All groups responded to this question; average group life was 4.2 years, with a range of 0.3 to 25 years. The subset of Japanese researchers had an average group life of 4.6 years, with a range of 2 to 10 years. Figure 5 shows the data on research group experience. The breakdown on group type (government, university, or commercial) is shown in Figure 6.

Question 3. "In general, what are the areas of CVD diamond film that you are investigating (i.e., deposition properties, chemistry, etc.)?"

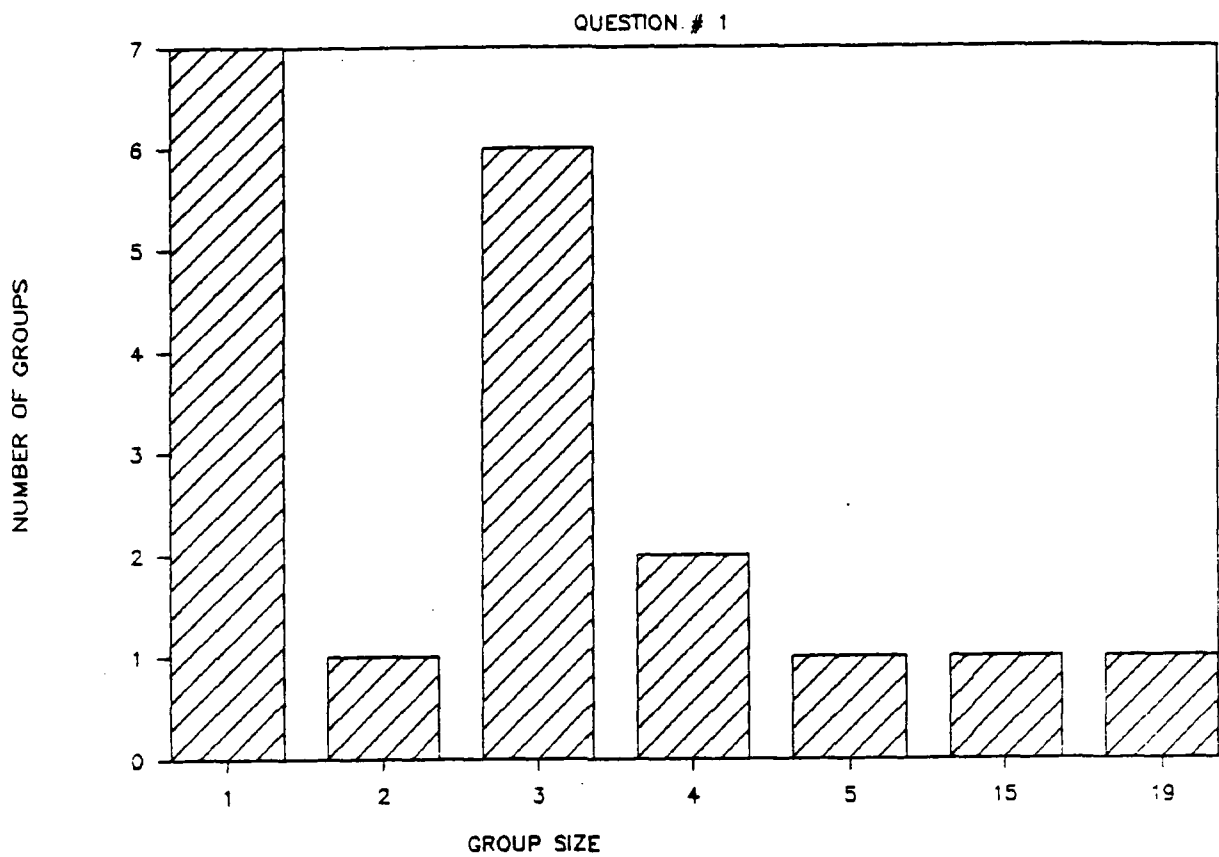


Figure 4. Research group size.

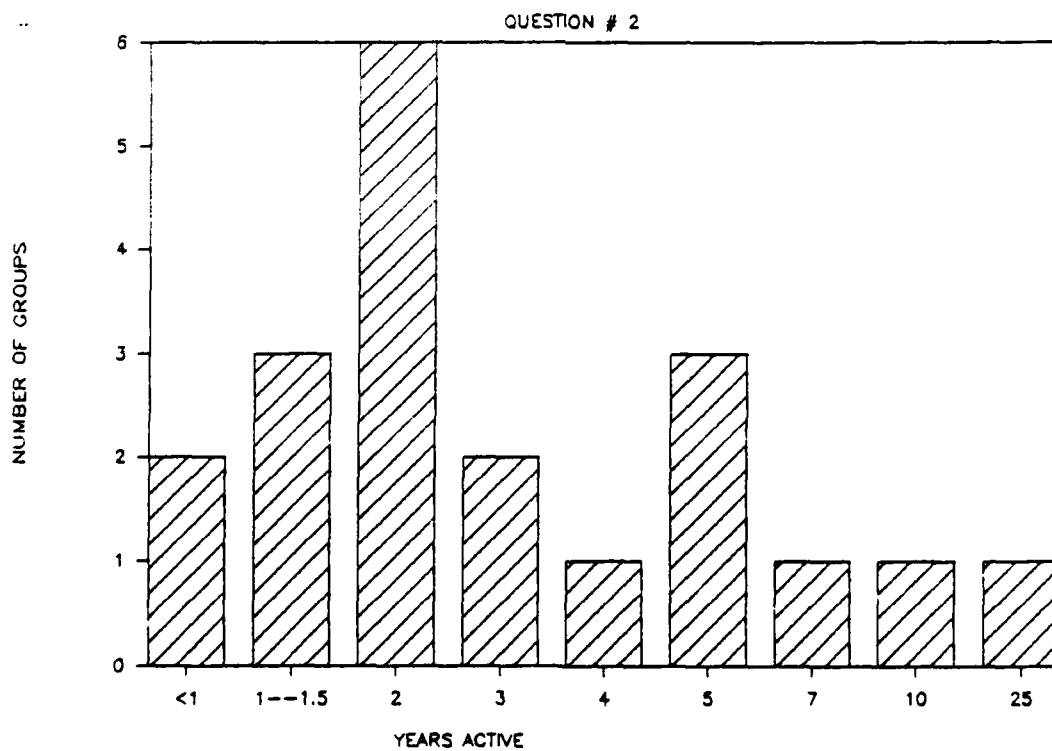


Figure 5. Group life.

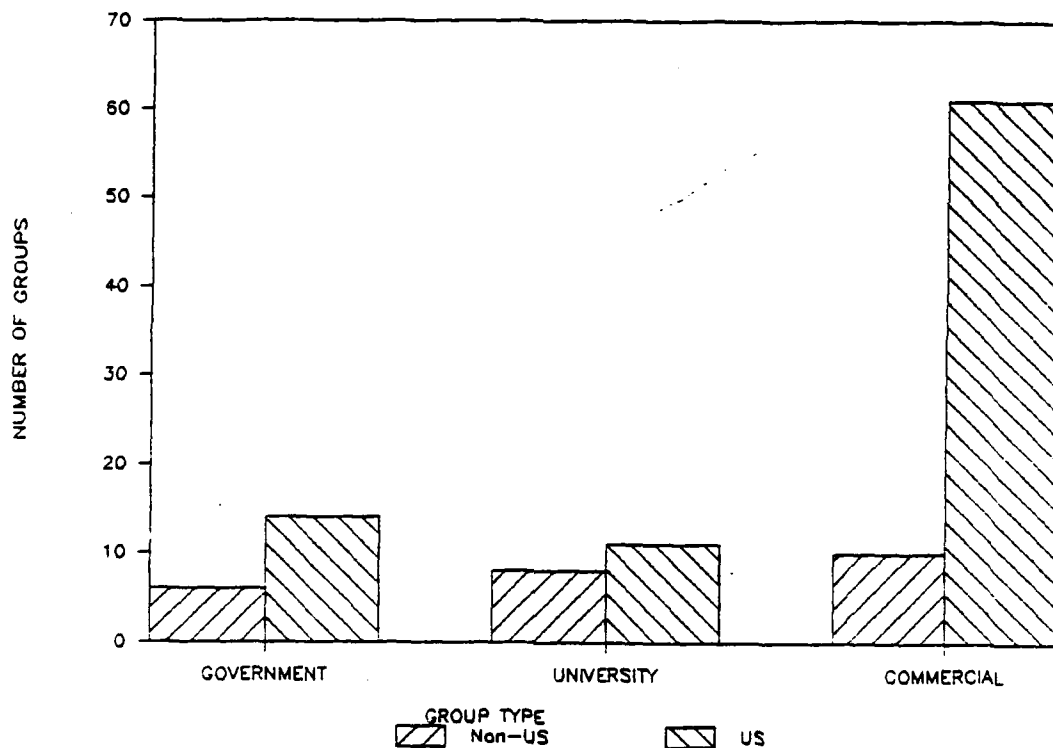


Figure 6. Types of group identified in survey.

All groups responding to the survey conduct diamond film synthesis. At least 90% of these make properties measurements on the resulting films. All groups are working toward at least one end application of their diamond films.

Question 4. "What properties of CVD diamond films have you measured and what were the results?"

At least 15 properties are used by one or more groups to characterize their diamond. The most widely measured property was hardness (9 groups), followed by electrical conductivity (8 groups), crystal structure and thermal conductivity (7 groups each). Six groups listed adhesion, while four groups listed mechanical strength and optical properties. Density and impurity concentration were each measured by three groups, and two groups listed dielectric constant and surface finish. Friction, porosity, microwave transmission, wear resistance, dielectric strength, oxidation resistance, and chemical resistance were listed by one group each.

Seventeen groups indicated they made one or more properties measurements. The average number of properties measured was 3.6, with a range from one to a maximum of ten, as shown in Figure 7.

Question #4

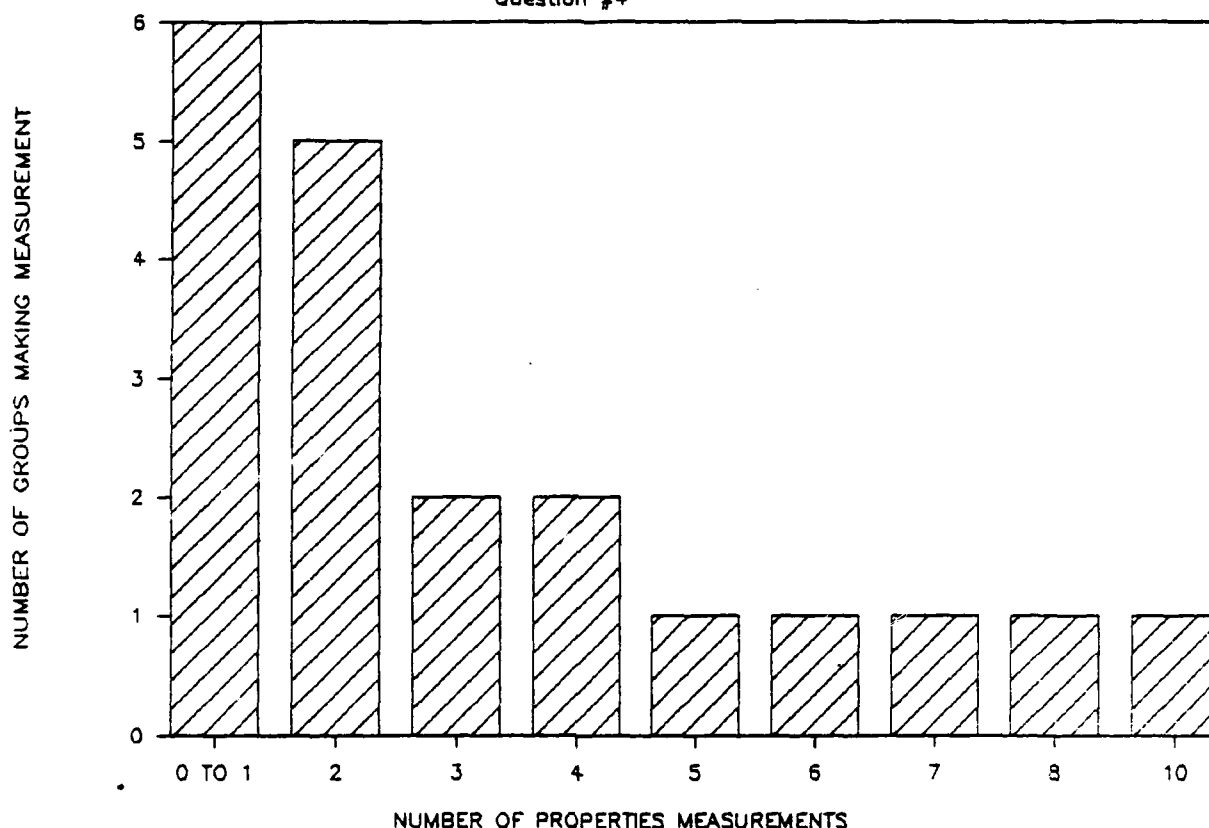


Figure 7. Number of properties measured.

Data provided directly on values of properties measured were more limited. Table 5 lists values provided directly in the survey (more extensive information was provided by reference in enclosed or referenced reports).

Five values of measured hardness were presented. Four were $\geq 10,000$ Kg mm⁻² Vickers hardness and one was 4500 to 5000 DPHN (where natural diamond = 6000 DPHN). Three values of thermal conductivity were listed: 800, 1000, and 1900 W, m⁻¹ K⁻¹ (copper is 400 WM⁻¹ K⁻¹). Electrical resistivity data were provided by five groups, covering the range from 10³ to 10¹⁶ ohm-cm. Dielectric constant was reported by two groups as 5.8 and 6 $\pm$ 0.5. One group reported a specific gravity of 3.5; one group reported a friction coefficient against steel in air of 0.08.

Question 5. "What are your typical deposition parameters?"

Data provided on operating conditions were limited. Deposition pressures for conventional plasma CVD diamond synthesis range from 1.5x10⁻⁴ to 200 torr. Ion deposition pressures are in the range of 10⁻⁶ torr. Substrate temperatures ranged from 150 C (ion) to 1000 C (max range for combustion). The "conventional" plasma processes operate with substrate temperatures from 600 to 1000 C.

Gas throughputs for the plasma processes range from 50 to 1,560 SCCM.

TABLE 5. Properties Data Provide Directly in Survey

Property	Values	Number of Respondents
1. Hardness	>10,000 Kg mm ⁻²	4
	4500-5000 DPHN	1
2. Thermal Conductivity	800 WM ⁻¹ K ⁻¹	1
	1000 WM ⁻¹ K ⁻¹	1
	1900 WM ⁻¹ K ⁻¹	1
3. Electrical Resistivity	10 ³ -10 ² Ohm cm	1
	10 ⁴ -10 ⁵ Ohm cm	1
	10 ⁸ -10 ¹⁰ Ohm cm	1
	10 ¹² Ohm cm	1
	>10 ¹⁴ Ohm cm	1
4. Coefficient of Friction (Against Steel in Air)	.08	1
5. Specific Gravity	3.5	1
6. Dielectric Constant	5.8	1
	6.0 ± 0.5	1

Only one response described the surface pretreatment process (polish with 0.25 -1 micron diamond powder, followed by atomic hydrogen etch). It should be noted that there is extensive literature available from the survey respondents and others which describe the processes in more detail.

Question 6. "What do you use as precursors?"

Half of the respondents indicated that methane was their carbon source at concentrations of 0.5 to 5%. Two indicated use of hydrocarbons and one indicated use of CO as a carbon source. The ion implant process uses a graphite target as the carbon source. Nearly half (45%) indicated use of hydrogen. One showed use of water as an alternate to H₂. None of the responses showed use of inert gas.

Question 7. "How do you produce the atomic hydrogen? Are you investigating other methods? What are they?"

A total of eight distinct processes were described, distributed as shown in Table 6. Most groups used more than one process; the average was between 2 and 3. Microwave excitation was the most common process, used by 60% of those responding. Hot filament ionization was used by 45% of the groups, and DC excitation was used by 25%. Laser dissociation was used only in conjunction with the ion beam process.

TABLE 6. Plasma Production Techniques and Reported Deposition Rates

<u>Process</u>	<u>Total Using Process</u>	<u>Total Providing Rate Data</u>	<u>Present Rate (micron/hr)</u>	<u>Projected Rate (micron/hr)</u>
Arc	2	-	-	-
Combustion	2	-	-	-
DC	5	3	10 - 200	40 - 1000
Electron Cyclotron Res.	1	-	-	-
Hot Filament	9	6	0.1 - tens	20 - 500
Ion	1	1	.02	30
Laser	*	-	-	-
Microwave	12	10	0.5 - 500	20 - 1000
Plasma and Others	3	-	-	-
RF	2	1	1.0	-

*Ion process also uses laser.

Question 8. "What are typical deposition rates you obtain for CVD diamond films? What rates do you expect to be able to obtain in two years? In five years? In ten years?"

The responses to this question are summarized in Table 6, condensed to rates obtained now and rates projected for the future, by synthesis process type.

Question 9. "What methods do you use to characterize the CVD diamond films?"

The respondents listed a total of 25 methods they used to characterize their diamond films. One group listed ten different measurements; the average number is 4.5, as shown in Figure 8.

Most groups (90%) used Raman spectroscopy for characterization. X-ray diffraction was used by 15 groups (75%). SEM characterization was the method next most used, by 14 groups (70%). Of the other 23 techniques, the next most mentioned was auger electron scanning, by 25%. Table 7 lists the measuring techniques indicated by the respondents.

Question 10. "Are you investigating CVD diamond particles or other forms such as fibers?"

Forty-eight percent (11) of the respondents indicated they were only involved with diamond films. Powders or particles were the area of interest for four groups (17%). The responses are summarized in Table 8.

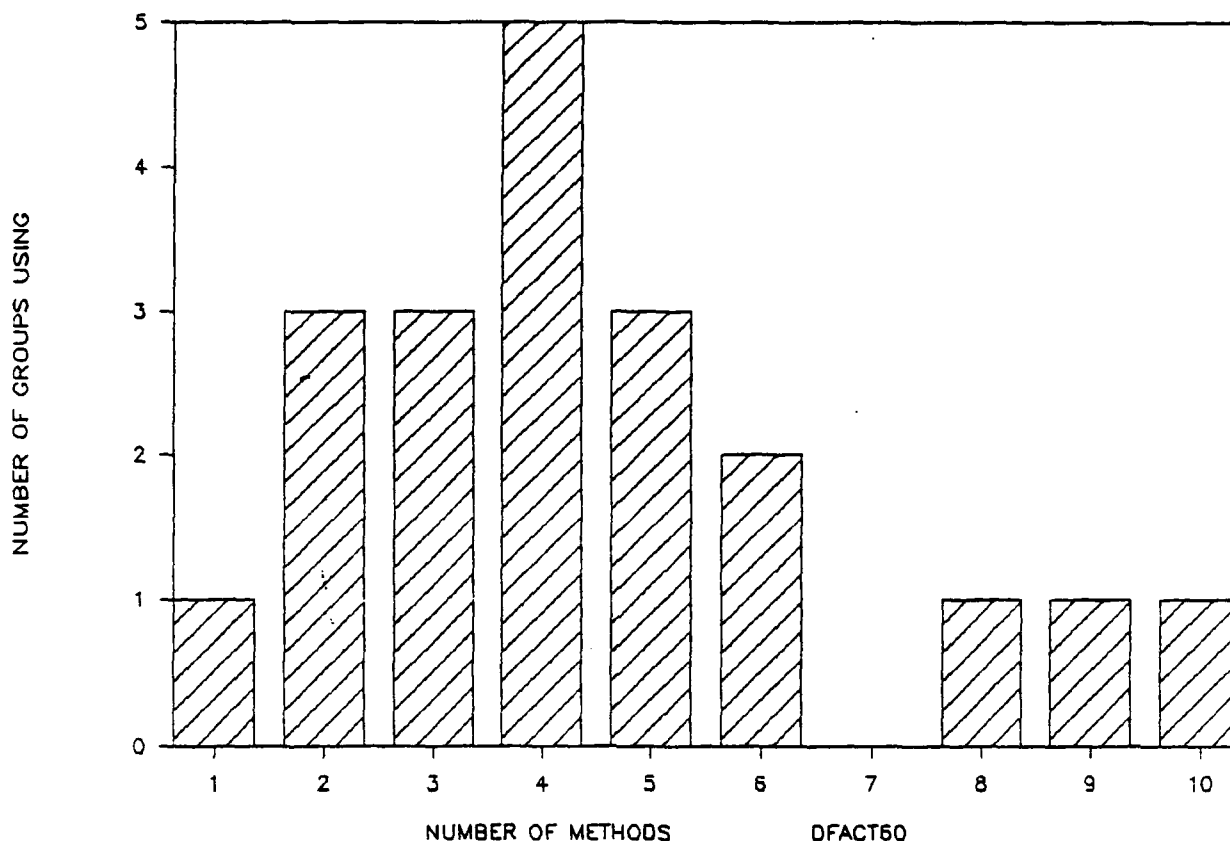


Figure 8. Number of characterization methods used.

TABLE 7. Characterization Techniques

<u>Technique</u>	<u>Number Using</u>
Auger Spectroscopy	6
Cathode Luminescence	1
Electrical Conductivity	4
Electron Energy Loss Spectroscopy (EELS)	2
Electron Reflection Defractometry (ERD)	3
Elemental Analysis	3
Hardness	3
IR Spectroscopy	1
Mechanical Strength	2
Microwave Transmission	1
Optical Microscopy	3
Optical Transmission	3
Profilimetry	1
Raman Spectroscopy	18
Reflective High-Energy Electron Diffraction (RHEED)	1
Scanning Electron Microscopy (SEM)	14
Thermal Conductivity	4
Transmission Electron Microscopy (TEM)	3
X-ray Photo Electron Spectroscopy (XPS)	1
X-ray Spectroscopy	15

TABLE 8. Type of Diamond Deposit Being Studied

<u>Form</u>	<u>Groups Studying</u>
Thin Films	20
Thick Films	2
Powders/Particles	4
Single Crystals	2
Sintered Compacts	1
Polycrystals	1
Other Than CVD	9

Question 11. "Do you have any interest in growing diamonds or diamond film by other than low-pressure CVD or PVD?"

Eleven respondents answered "no" or "no comment." Nine responded positively, one of these indicating by combustion and another by "hollow hydrocarbon cathode."

Question 12. "What is the minimum deposition temperature you have used to deposit diamond (not DLC) films?"

The range indicated for "conventional" processes was 370 to 950 C, with an average of about 720 C. The range of minimum temperature distribution is shown in Figure 9. The minimum for the ion implantation process is 100 C.

Question 13. "What applications of diamond film are you working on?"

Nineteen respondents indicated that they were working on specific applications and listed them, one did not respond, and one indicated that the applications were proprietary. A total of 42 applications were cited, for an average of two applications per group. The results, when grouped by major category, are shown in Table 9. The specific applications named by the respondents are listed in Table 10.

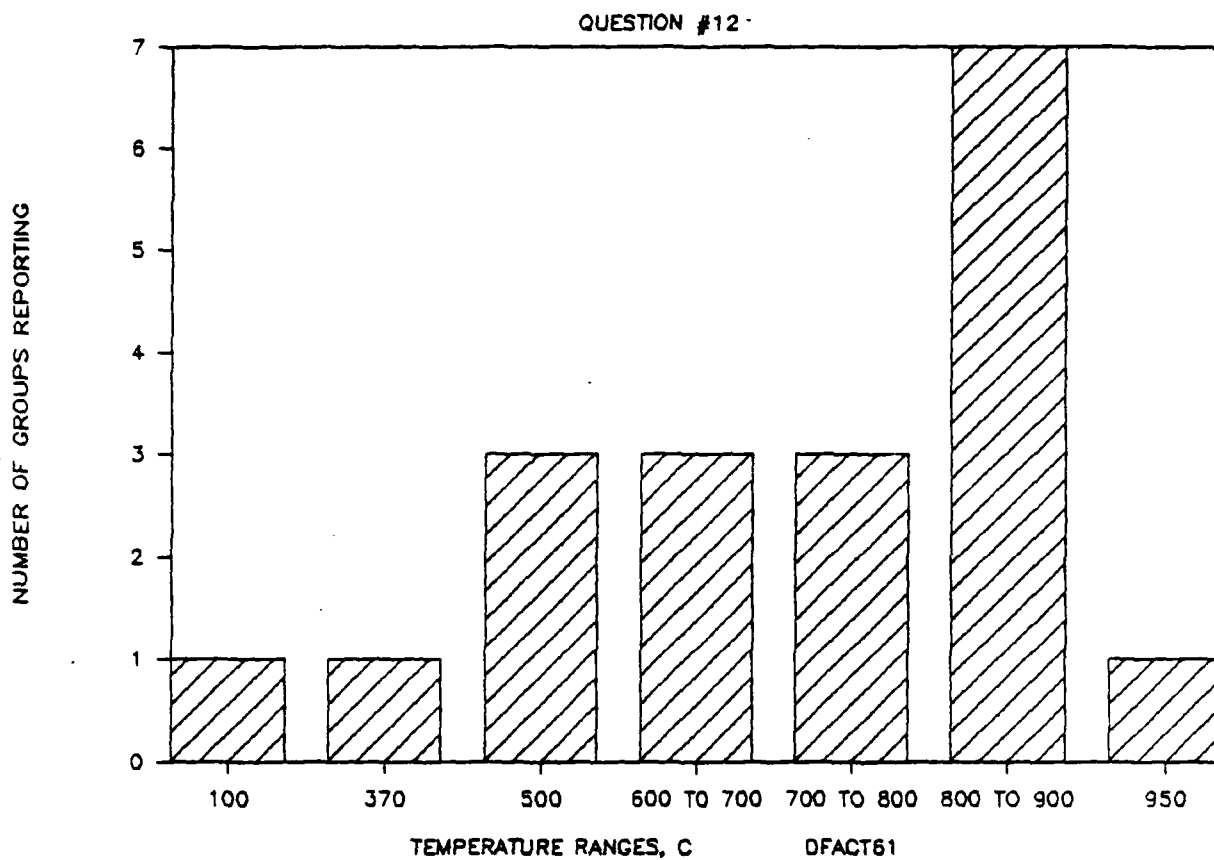


Figure 9. Minimum deposition temperature range.

TABLE 9. Diamond Film Application Area

<u>Application</u>	<u>Number</u>
Mechanical	20
Electrical	9
Thermal	5
Optical	5
Corrosion Protection	<u>3</u>
	42

TABLE 10. Specific Applications Named by Respondents

<u>Application</u>	<u>Concept</u>	<u>Development</u>	<u>Production</u>	<u>Other</u>
Biomedical Coatings		1		
Computer Disks		1		
Corrosion-Resistant Coatings				1
Ceramic Tool Coatings		1		
Hard Coatings	1			
Heat Sinks	2	2		1
Lenses		1		
Machine Parts		1		
Magnetic Tape Heads		1		
Microwave Windows		1		
Optical and IR Windows	1			
Semiconductor Electronic Devices	1	3		3
Sintered Powders	1			
Speaker Diaphragms			1	
Thermistors			1	
Tool Coatings	1	2	3	2
Vapor Barriers				1
Wear Applications		1		
X-ray Windows			1	
	<u>7</u>	<u>17</u>	<u>7</u>	<u>9</u>

3.2 DIAMOND FILM SYNTHESIS PROCESSES

CVD diamond is formed by interaction of a carbon-containing compound, such as methane, on a hot surface in the presence of a species, such as atomic hydrogen, which can react preferentially to block the deposition of graphite. At least ten methods have been identified for producing the CVD plasma environment, as listed in Table 11. All of these, except direct laser discharge and UV radiation, were in use by one or more of the survey respondents. Their estimated developmental status is indicated in the table.

A typical CVD process using DC plasma discharge is shown schematically in Figure 10. Very simplified schematics of six of the processes are shown in Figures 11 and 12. The probable stages in development of a diamond film by such a process are shown in Figure 13. A number of process variables can be adjusted to change the quality of the resulting deposits. This is illustrated in Figure 14, where a wide range of crystallite forms from the same basic DC discharge apparatus are illustrated.

Very preliminary estimates of the comparative capabilities and costs of nine of the processes were made and are presented in Table 12. These estimates were made by Crystallume based on their direct experience with the DC and microwave processes and on information available to them or on reasonable projections for the other processes. The results are indicative of the relative magnitudes of performance and cost on a consistent basis. It is probable that, given the proper motivation and development, orders of magnitude decreases could be made in some of the production cost parameters.

TABLE 11. Diamond Film Synthesis Processes

<u>PROCESS TYPE</u>	<u>STATUS</u>
ARC DISCHARGE	DEVELOPMENT
COMBUSTION	DEVELOPMENT
DC PLASMA	PRODUCTION
ELECTRON CYCLOTRON RESONANCE	DEVELOPMENT
ION IMPLANTATION	PRODUCTION
LASER DISCHARGE	DEVELOPMENT
MICROWAVE PLASMA	PRODUCTION
RF PLASMA	DEVELOPMENT
THERMAL PLASMA	DEVELOPMENT
UV RADIATION	DEVELOPMENT

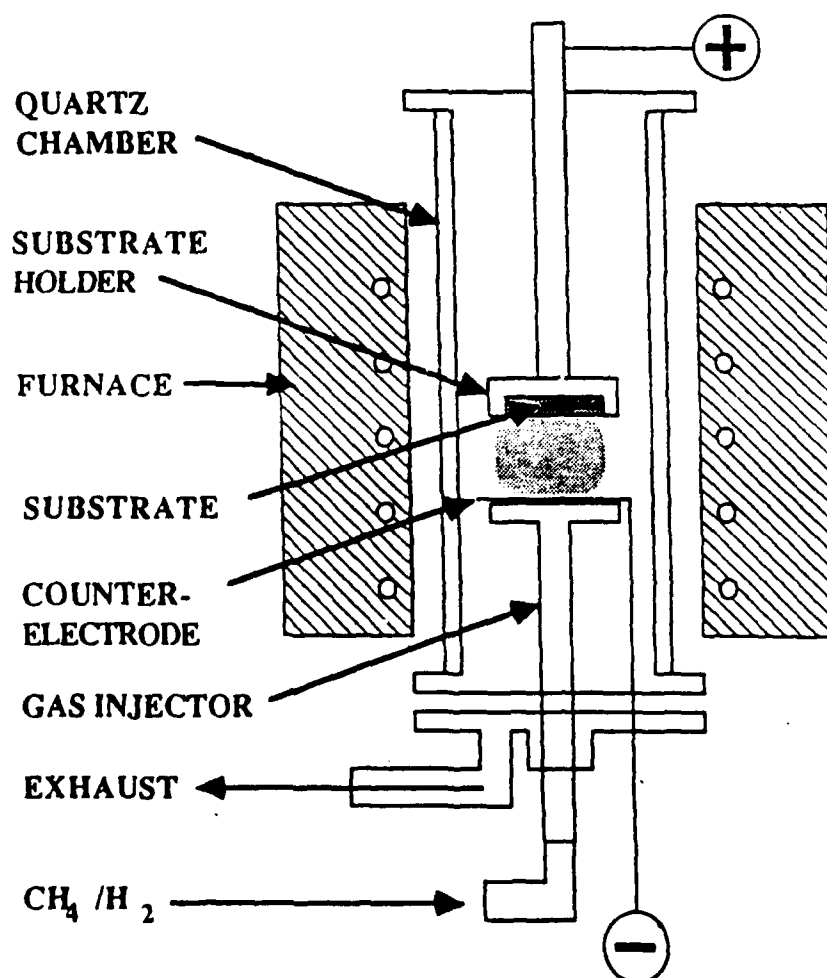


Figure 10. Schematic of DC discharge CVD diamond apparatus.

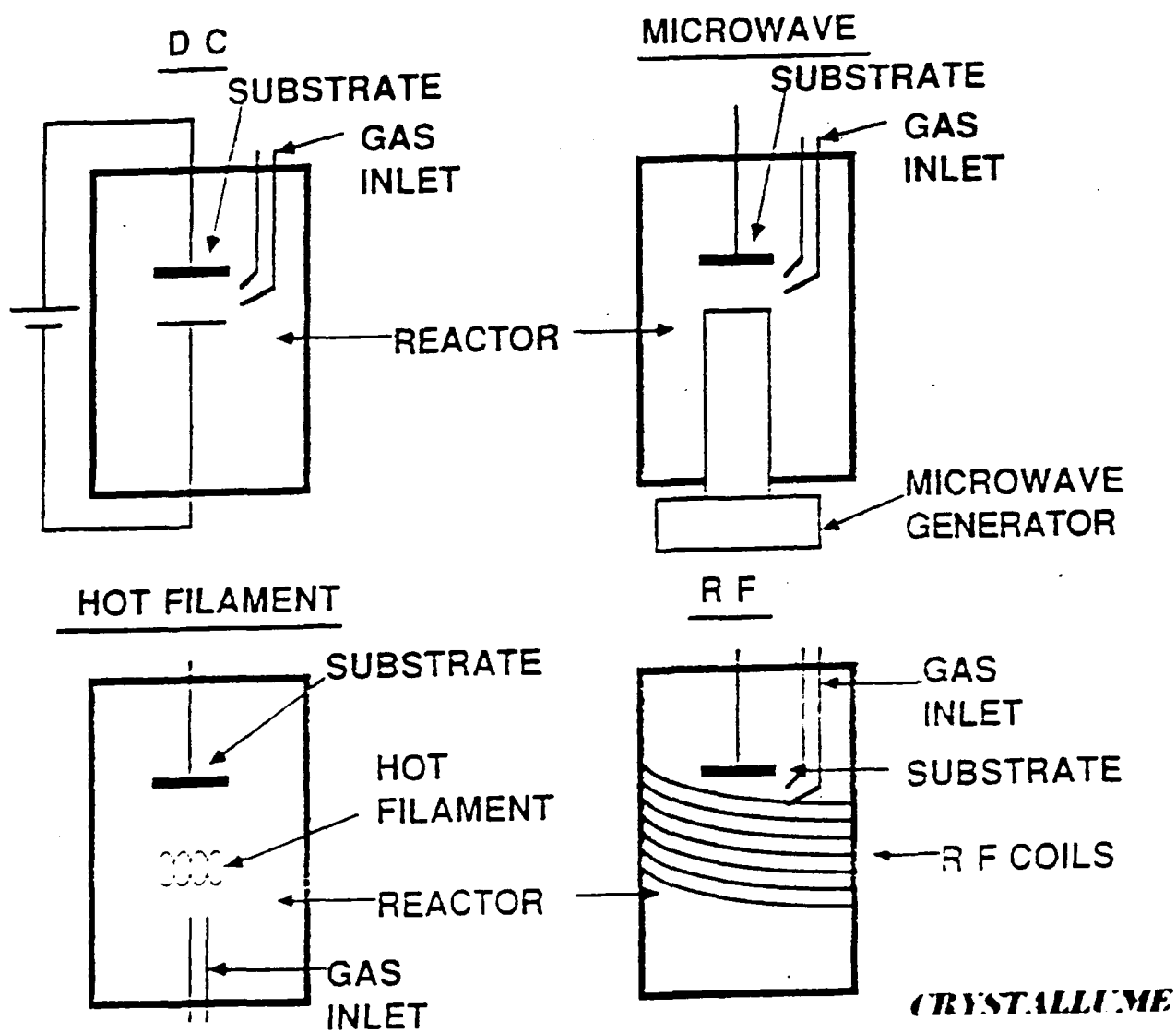
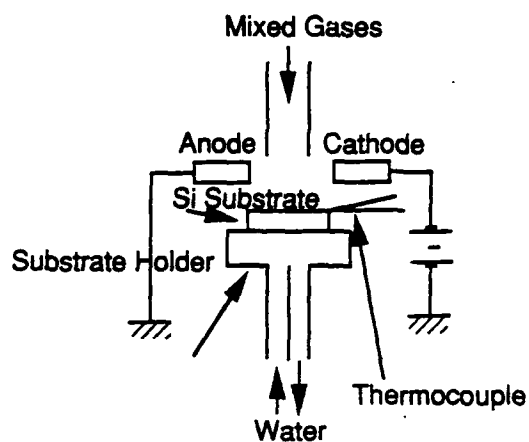


Figure 11. Approaches for diamond film synthesis.

- Arc Discharge Process
- growth rate $>200\mu/\text{hour}$
- area unknown
- good film quality (Raman Spectrum)



- Oxyacetylene Torch Process
- growth rate $>100\mu/\text{hour}$
- area $>5 \text{ sq. mm}$
- film quality questionable

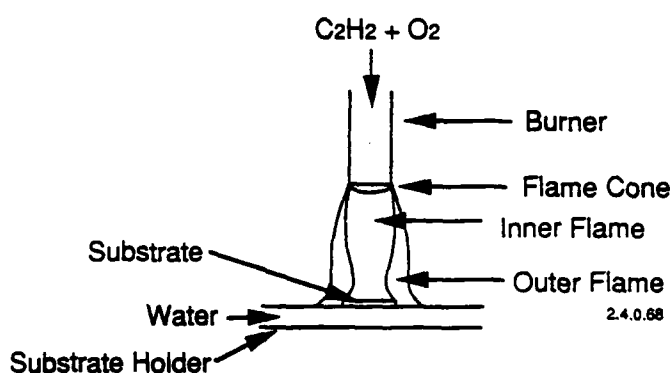


Figure 12. Two recently developed synthesis processes (ref 3).

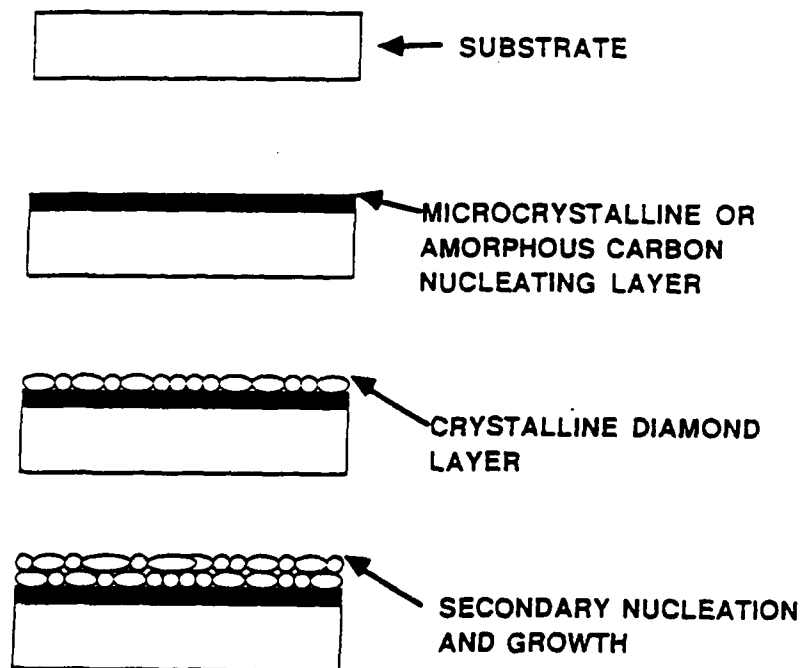
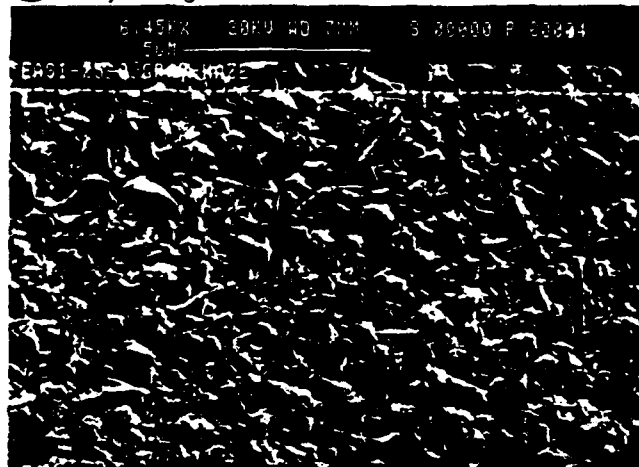
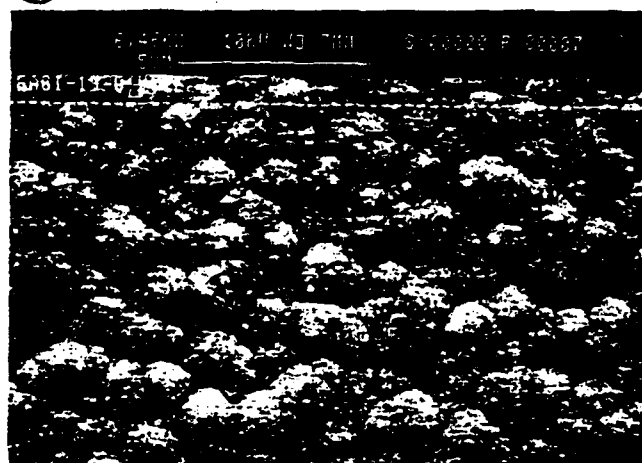


Figure 13. Suggested model for the nucleation of crystalline diamond films on single crystal substrates.

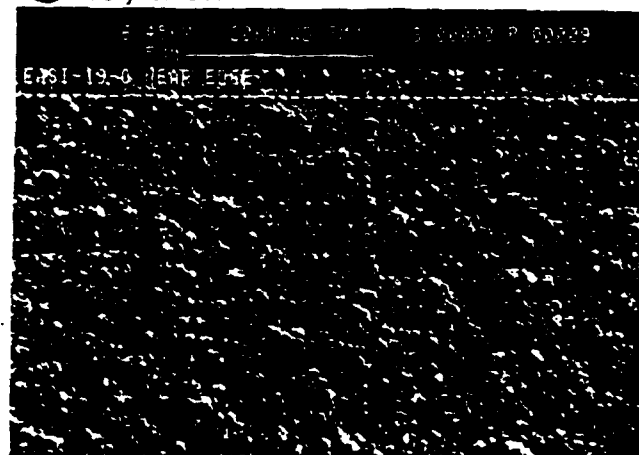
(A) Very Rough



(B)



(C) Very Smooth



log 88.486

Figure 14. Scanning electron photomicrographs of diamond film surfaces.

TABLE 12. Diamond Synthesis Process Estimates Page 1 of 2

	A	B	C	D	E	F
1	Calculations for 1990	ARC DISCH.	COMBUSTION	DC PLASMA	ECR μ WAVE	MICROWAVE
2						
3	INPUTS					
4	Production Development cost, \$/year	\$1,500,000	\$1,000,000	\$1,500,000	\$1,500,000	\$1,000,000
5	Production Development time, years	4	3	2	2	1
6						
7	Deposition Rate, μ /hour	300	100	20	10	25
8	Deposition Diameter, inches	3	6	12	30	10
9						
10	Production Machine Cost, \$/each	\$400,000	\$250,000	\$400,000	\$600,000	\$500,000
11	Machine lifetime, years	2	5	2	4	4
12	Estimated Operating Cost, \$/hr	\$225	\$150	\$225	\$200	\$188
13						
14						
15	OUTPUTS					
16	Development Program cost, \$	\$6,000,000	\$3,000,000	\$3,000,000	\$3,000,000	\$1,000,000
17	Deposition Area, sq. inches	7.1	28.3	113.1	706.9	78.5
18	Deposition Area, sq. cm	45.6	182.4	729.7	4560.4	506.7
19	Deposition Rate, gm/hour	4.8	6.5	5.2	16.1	4.5
20						
21	Estimated 1990 Deposition Cost, \$/sq. cm/hr	\$4.93	\$0.82	\$0.31	\$0.04	\$0.37
22	Estimated 1990 Deposition Cost, \$/gm	\$46.47	\$23.23	\$43.56	\$12.39	\$41.82
23	Estimated 1990 Deposition Cost, \$/kg	\$46,469.31	\$23,234.66	\$43,564.98	\$12,391.82	41,822.38
24						
25	Time required to coat 1 sq ft to 1 μ thick, minutes	4.07	3.06	3.82	1.22	.40
26						
27	Estimated 1990 Cost of Coating 1 sq ft to 1 μ , \$/sq ft	\$15.28	\$7.64	\$14.32	\$4.07	13.75
28						
29						
30	Estimated 1990 Commercial Production Value, \$/gm	\$100.00	?	\$300.00	465.00	150.00
31	(except ion beam, 1995 value)					

M70F/Tab 3.2.2

TABLE 12. Diamond Synthesis Process Estimates Page 2 of 2

	G	H	I	J	K
1	Calculations for 1990	ION BEAM	LASER-ASSIST	THERMAL	UV-ASSIST
2					
3	INPUTS				
4	Production Development cost, \$/year	\$3,000,000	\$2,000,000	\$1,000,000	\$2,000,000
5	Production Development time, years	5	3	2	3
6					
7	Deposition Rate, μ /hour	0.5	1	20	1
8	Deposition Diameter, inches	8	8	24	12
9					
10	Production Machine Cost, \$/each	\$3,000,000	\$1,500,000	\$150,000	\$500,000
11	Machine lifetime, years	5	2	3	2
12	Estimated Operating Cost, \$/hr	\$425	\$500	\$150	\$250
13					
14					
15	OUTPUTS				
16	Development Program cost, \$	\$15,000,000	\$6,000,000	\$2,000,000	\$6,000,000
17	Deposition Area, sq. inches	50.3	50.3	452.4	113.1
18	Deposition Area, sq. cm	324.3	324.3	2918.6	729.7
19	Deposition Rate, gm/hour	0.1	0.1	20.7	0.3
20					
21	Estimated 1990 Deposition Cost, \$/sq. cm/hr	\$1.31	\$1.54	\$0.05	\$0.34
22	Estimated 1990 Deposition Cost, \$/gm	\$7,406.05	\$4,356.50	\$7.26	\$968.11
23	Estimated 1990 Deposition Cost, \$/kg	\$7,406,046.94	\$4,356,498.20	\$7,260.83	\$968,110.71
24					
25	Time required to coat 1 sq ft to 1 μ thick, minutes	343.77	171.89	0.95	76.39
26					
27	Estimated 1990 Cost of Coating 1 sq ft to 1 μ , \$/sq ft	\$2,435.07	\$1,432.40	\$2.39	\$318.31
28					
29					
30	Estimated 1990 Commercial Production Value, \$/gm	\$11,600.00	?	?	?
31	(except ion beam, 1995 value)				

1/7/95/1646 3.2.2

Present processes, such as DC and microwave discharge deposition, are operated much like microelectronic chip production. Figures 15 and 16 illustrate a typical synthesis form, a 4-in. wafer, and show the uniformity of composition and deposition thickness achieved.

As noted in Section 3.1, Raman spectra are universally used to characterize diamond films since they can distinguish between diamond and graphite. Raman spectra for CVD diamond and natural diamond are compared in Figure 17.

If a need arose for continuous production of diamond film in large quantities, there are techniques which should be adaptable. Vacuum plasma sputtering processes are in routine production of coatings on continuous films, both nonmetallic and metallic, which are meters wide and kilometers long. Such a process could provide inexpensive diamond film for layered composite structures for engineering applications, for example.

Recent European processes for production of CVD diamond particles produce crystal deposits on filaments like beads on a string, which are then stripped off for use in cutting tools and abrasives.

A barrier to use of diamond film is process incompatibility with the substrate. This can be due to excessive process temperature, adverse chemical attack such as hydride formation, inadequate nucleation, or inadequate bonding. Some of these deficiencies may be cured by flash-coating the surface with a compatible material before diamond deposition. Nucleation and bonding sites are typically provided by scratching the surface microscopically with fine diamond powder.

Diamond film adherence on metal surfaces is thought to be enhanced by formation of an initial carbide layer. Carbide formation characteristics of a range of elements are shown in Table 13. It should be noted, however, that this is not a sufficient criterium. Iron, for example, forms a stable carbide but is not a good substrate for reasons that are not well understood.

Actual coating experience on a limited set of metals, oxides (Al_2O_3 and SiO_2), carbides (SiC , TiC , and WC), and nitrides (BN , SiN), is shown in Table 14.

3.3 PROPERTIES OF DIAMOND FILM

An extensive properties literature exists for natural diamond. Only a few of these properties have been unambiguously measured for diamond film. Properties listed below have been gathered from the literature, from the diamond film technology survey, from measurements in this program, and from other programs which are in progress.

3.3.1 Published Literature Data--A summary of properties for natural diamond and CVD diamond is given in Table 15. The data presentation is based on properties summary given in Ref. 4, which has been extensively updated.

Some of the more interesting properties of diamond are compared to those of other engineering materials in Tables 16 and 17 (from Ref. 5). This highlights the unusual friction, hardness, thermal conductivity, modulus, and semiconductor capabilities of diamond.

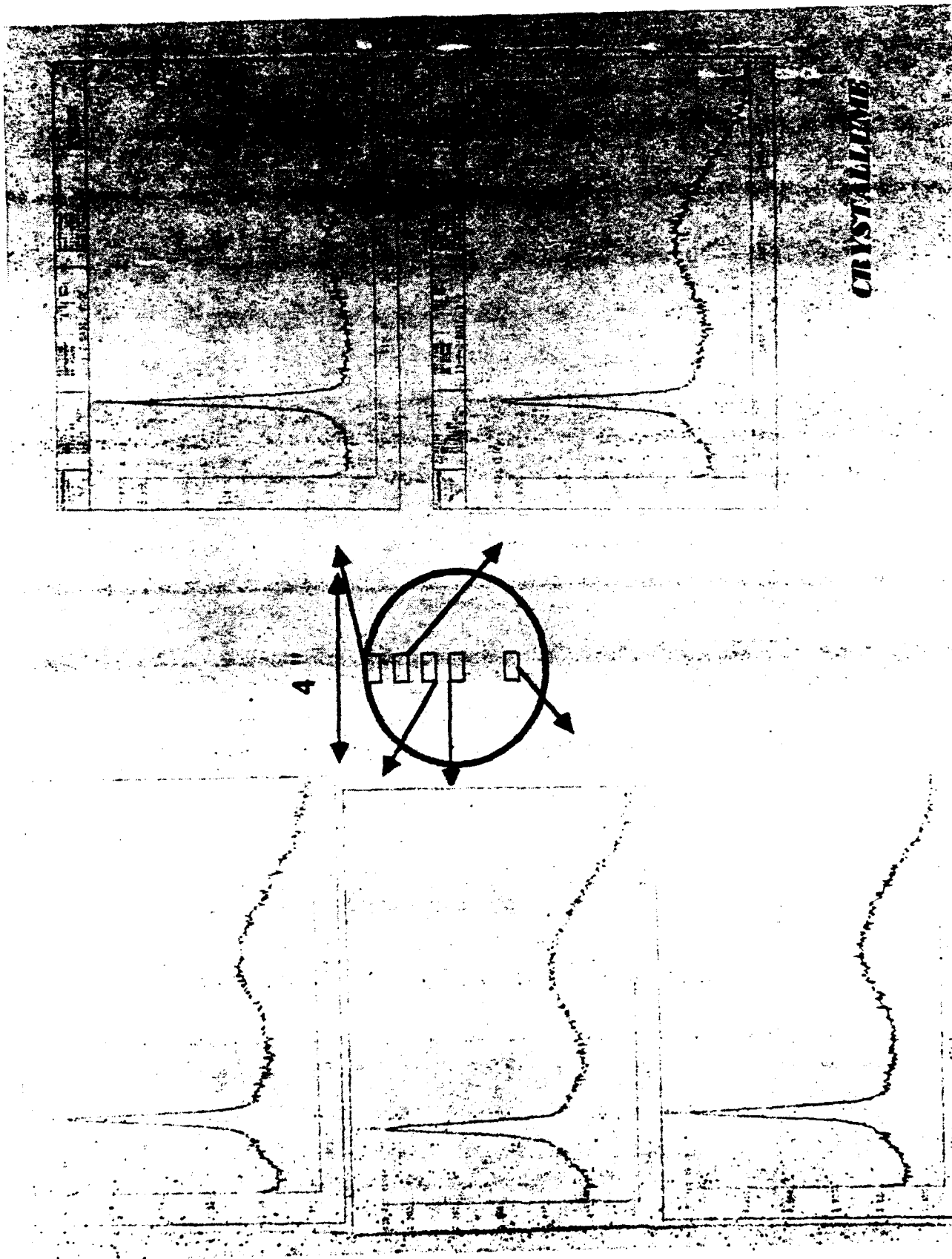


Figure 15. Common spectra show coating uniformity.

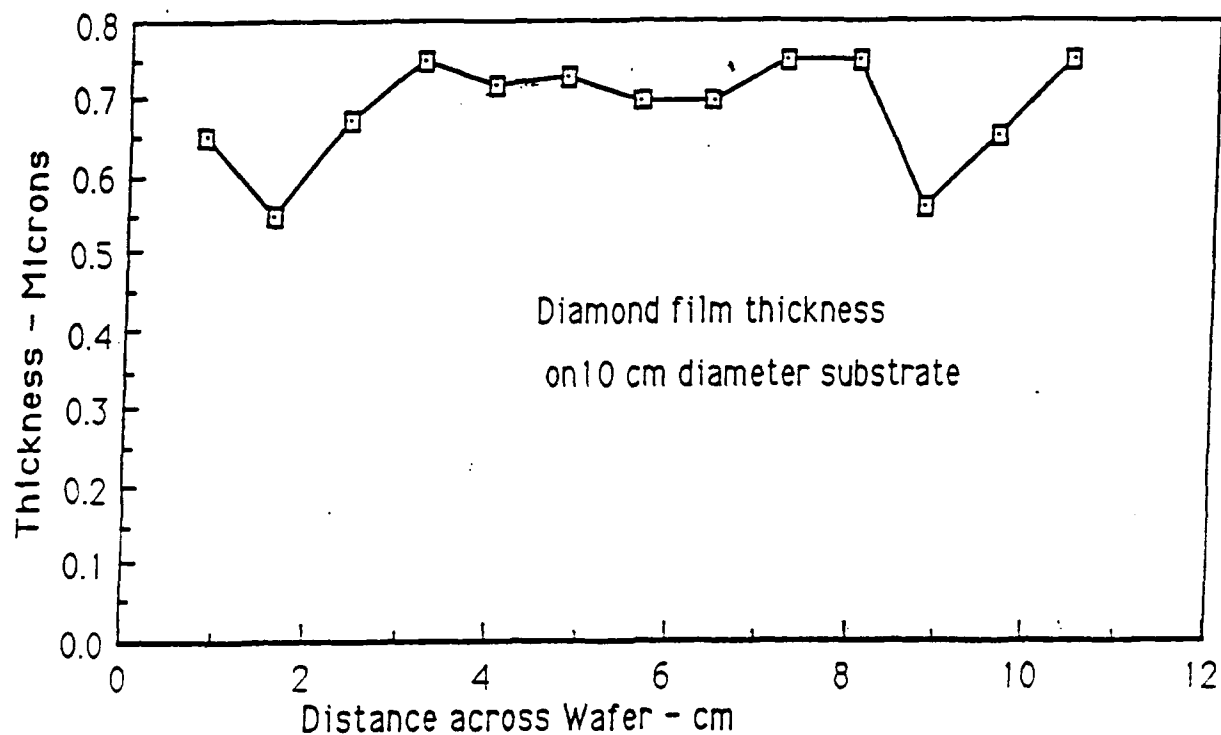


Figure 16. Thickness uniformity.

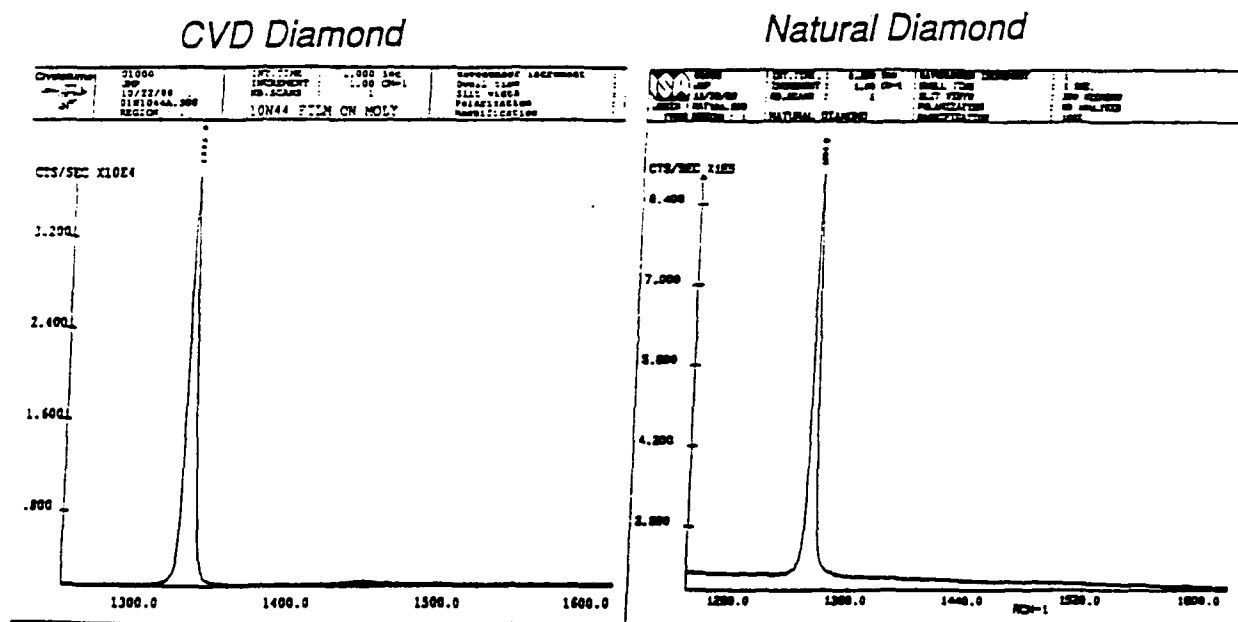


Figure 17. Raman spectra of CVD and natural diamond.

TABLE 13. Potential Diamond Film Adherence Based on Substrate

SUBSTRATE	CARBIDE	COMMENT
Aluminum	Al ₄ C ₃	Carbide decomp in water
Beryllium	Be ₂ C	Carbide decomp in water
Carbon	--	
Chromium	Cr ₃ C ₂	Stable carbide
Cobalt	--	
Copper	--	
Germanium	--	
Gold	--	
Hafnium	HfC	Stable carbide
Iridium	--	
Iron	Fe ₃ C	Stable carbide
Magnesium	--	
Manganese	Mn ₃ C	Carbide decomp in water
Molybdenum	Mo ₂ C	Stable carbide
Nickel	Ni ₃ C	?
Niobium	NbC	Stable carbide
Palladium	--	
Platinum	--	
Plutonium	--	
Rhenium	--	
Rhodium	--	
Selenium	SeC ₂	Low melting point
Silicon	SiC	Stable carbide
Silver	--	
Tantalum	TaC	Stable carbide
Thorium	ThC ₂	Stable carbide
Titanium	TiC	Stable carbide
Tungsten	WC	Stable carbide
Uranium	UC ₂	Carbide decomp in water
Vanadium	VC	Stable carbide
Zirconium	ZrC	Stable carbide

TABLE 14. Data on Diamond Film Deposition and Adherence as a Function of Substrate

Aluminum – (C) Sputtered aluminum (200A on GaAs wafer) works well. No data on convention aluminum specimens.

Alumina – (C) Adherent diamond deposits.

Beryllium – (C) Rolled Be foil gives inconsistent results; sometimes diamond, sometimes DLC, probably because of refractory surface oxide.

Boron Nitride – Diamond nucleates, grows and sticks well

Carbon – (C) Diamond has been deposited on carbon-carbon samples. Adhesion was poor. Diamond nucleates, grows and adheres to graphite.

Copper – (C) Diamond nucleates and grows, does not adhere.

Germanium – (C) Diamond nucleates and grows, does not adhere.

Iron – (C) Poor adhesion has been obtained.

Molybdenum – Diamond nucleates, grows, and sticks well.

Nickel – Literature shows attempts to deposit unsuccessful.

Niobium – (C) Adherent diamond grown successfully on Nb - 1% Zr alloy.

Silicon – (C) Diamond nucleates, grows, and sticks well.

SiC, Si₃N₄ (amorphous) – (C) Adherent diamond deposits.

SiO₂ – (C) No deposits.

Tantalum, Titanium, Tungsten – (C) Diamond nucleates, grows, and sticks well. Variable results have been obtained with titanium alloy (Ti6Al4V).

TiC, WC – (C) Adherent diamond deposits.

Zirconium – See Niobium above.

Note: (C) = Crystallume experience.

M7/DF/Tab1e3.2-4

TABLE 15. Properties of Natural and Synthetic Diamond, Page 1 of 2

CLASS	PROPERTY	UNITS	NAT. DIAMOND	SYN. DIAMOND
Chemical	Bond type	% covalent	100	
Chemical	Catalytic activity			
Chemical	Isoturities			
Chemical	Molecular weight	gm/mole	12.0111	
Chemical	Reactivity			
Electronic	Band gap	eV	5.4	5.3
Electronic	Breakdown field	V/cm		>10E6
Electronic	Carrier lifetime	microsec		.4--.6
Electronic	Dielectric constant	--	5.58	5.3
Electronic	Electroacoustical attenuation factor	M sec-1		
Electronic	Electromechanical coupling coef.	--		
Electronic	Electron Mobility			
Electronic	Loss tangent			
Electronic	Mobility, hole			
Electronic	Resistivity, Ib	Ohm-cm	10E12--10E16	>10E16
Electronic	Resistivity, IIa	Ohm-cm	10E4--10E12	
Electronic	Resistivity, IIb	Ohm-cm	10-10E3	
Electronic	Work function			
Mechanical	Adherence	dynes/cm2		
Mechanical	Compressibility	cm2/dyne	2.3x10E-13	
Mechanical	Compressive strength	dynes/cm2	9.65x10E11	
Mechanical	Damping capacity			
Mechanical	Dislocation mobility temp	C		
Mechanical	Elastic constant, C11	dynes/cm2	107.6x10E11	
Mechanical	Elastic constant C12	dynes/cm2	12.3x10E11	
Mechanical	Elastic constant C44	dynes/cm2	57.2x10E11	
Mechanical	Fracture mode	--	on {111} planes	
Mechanical	Fracture toughness			
Mechanical	Friction coefficient, dynamic			
Mechanical	Friction coefficient, static			
Mechanical	Hardness	Kg/mm2	>9000	10000 ±
Mechanical	Hardness	Woodell	42.5	
Mechanical	Phonon spectra	cm-1		1333
Mechanical	Shear strength	dynes/cm2		
Mechanical	Tensile strength	dynes/cm2	3.45x10E10	3.45 ± 10E10
Mechanical	Wear rate	mm3/a		10E-17
Mechanical	Young's Modulus	dynes/cm2	10.35x10E12	
Optical	Band Gap, direct	eV	7.0	
Optical	Band gap, indirect	eV	5.47	
Optical	Dispersion			
Optical	IR spectra			
Optical	IR transmission			
Optical	Refractive index (2589.3nm)	--	2.417	
Optical	UV spectra			
Optical	UV transmission			
Optical	Valance band width	eV	21.5	
Optical	Visible spectra			
Optical	Visible transmission			
Optical	X-ray Transmissivity			
Physical	Atoms/unit cell	Same	8	

TABLE 15. Properties of Natural and Synthetic Diamond, Page 2 of 2

CLASS	PROPERTY	UNITS	NAT. DIAMOND	SYN. DIAMOND
Physical	Cleavage	--	{111}	
Physical	Crystal habit	--	{111}, {110}	
Physical	Crystal system	--	Cubic	
Physical	Crystallinity			
Physical	Defect density			
Physical	Density	gm/cm ³	3.515	
Physical	Diffusion coefficient	cm ² /sec		6.4x10E-12
Physical	Formula	--	C	
Physical	Ionic distance	Å	1.54 (C-C)	
Physical	Lattice constant	Å	3.56696	
Physical	Space group	--	Fd3m	
Physical	Structure type	--	Diamond	
Physical	Twinning	--	{111}	
Thermal	Conductivity @25C	Watt cm-1 C-1	20	19
Thermal	Debye temperature @0K	K	2220	
Thermal	Debye temperature @0-900C	K	1860	
Thermal	Linear expansion, @400C	cm cm-1 C-1	3.5x10E-6	
Thermal	Linear expansion, @750C	cm cm-1 C-1	4.5x10E-6	
Thermal	Linear expansion, @78C	cm cm-1 C-1	1.5x10E-6	
Thermal	Specific heat @150K	cal mol-1 deg C-1	0.24	
Thermal	Specific heat @289K	cal mol-1 deg C-1	1.46	
Thermal	Specific heat @400K	cal mol-1 deg C-1	2.52	
Thermal	Stability, onset of oxidation in air	C	600	
Thermal	Stability, onset of graphitization in vacuum	C	1400-1700	
Thermodynamic	Energy, cohesive	k cal mole-1	320	
Thermodynamic	Energy, lattice (type I)	k cal mole-1	9400	
Thermodynamic	Energy, surface, e111	ergs cm-2	5378	
Thermodynamic	Energy, surface, s111	ergs cm-2	5270	
Thermodynamic	Entropy, @ 298K	e.u. gm atom-1	0.59	
Thermodynamic	Heat of formation, @ 298K	k cal mole-1		
Thermodynamic	Melting point	K	4000 ± 130 kb	
Thermodynamic	Transform., cubic to hex	--		
Thermodynamic	Transform., hex to Wurtzite	--		

± Measurements from Phase III

TABLE 16. Comparison of Material Properties

Coefficient of Friction (Like or like)

<u>Material</u>	<u>Value</u>
Diamond	0.05-0.15
Teflon	0.10
Graphite (clean)	0.10
Graphite (outgassed)	0.5-0.8
Sapphire	0.15
Titanium	0.60
Aluminum	1.9
Steel	0.58
Tungsten Carbide	0.17

Hardness

<u>Material</u>	<u>Value (Kg/mm²)</u>
Diamond	9,000
Cubic Boron Nitride	4,500
TiN	3,000
SiC	2,500
Tungsten Carbide	1,900

Thermal Conductivity

<u>Material</u>	<u>Value (W/cm/degree K)</u>
Natural Diamond (max.)	20.0
CVD Diamond	10.0 to 19
<u>Electrical Conductors</u>	
Silver	4.3
Copper	4.0
Graphite	2.1
<u>Electrical Insulators</u>	
SiC	2.7
Beryllium Oxide	2.2
AlN	1.7
Al ₂ O ₃	0.4
Sapphire	0.3

Young's Modulus

<u>Material</u>	<u>Value (10¹² dynes/cm²)</u>
Diamond	10.35
Silicon Carbide	7.0
Silicon Nitride	3.85
Silicon	1.9
Boron Nitride	1.5-2.51

TABLE 17. Semiconductor Comparisons

Property	Silicon	GaAs	Diamond
Bandgap (eV)	1.1	1.43	5.45
Hole Mobility (cm ² -N-sec)	600	400	1,600
Electron Mobility (cm ² -N-sec)	1,500	8,500	1,900
Breakdown Voltage (volts)	5x10 ⁶	6x10 ⁶	1x10 ⁷
Resistivity (Ohm-cm)	103	108	1,013
Thermal Conductivity (w-cm ⁻¹ c ⁻¹)	1.45	0.46	20
Electron Velocity (High Field) (cm sec ⁻¹)	1x10 ⁷	1x10 ⁷	2.7x10 ⁷
Dielectric Constant (-)	11	12.5	5.5
Lattice Constant (Å)	5.43	5.65	3.57
Hardness (Kg/mm ²)	103	600	9,000
Refractive Index (-)	?	3.4	2.4
Thermal Coefficient (cm-cm ⁻¹ -c ⁻¹)	2.6x10 ⁻⁶	5.9x10 ⁻⁶	1.1x10 ⁻⁶
Work Function (eV)	4.8	4.7	4.8
Carrier Lifetime (sec)	2.5x10 ⁻³	10 ⁻⁸	n/a
Melting Point (°C)	1,420	1,238	n/a
Pf ² z (Figure of merit)	9x10 ²³	6x10 ²⁴	7x10 ²⁷

M7/DF/Table17

3.3.2 Measurements Made in This Program--The results of properties measurements made during this program are summarized in Table 18. The basis for these measurements is described in Section 5.

Measurements reported in the technology status survey are presented in Section 3.1, Question 4.

TABLE 18. Summary of Measurements Made in This Program

<u>Parameter</u>	<u>Value</u>
Hydrogen Diffusion Rate	Less than 3.0x10 ⁻¹¹ torr-cm ² -hr ⁻¹
Hardness	About 10,000 Kg-mm ⁻²
Thermal Cycle Adhesion	At least 100 cycles from ambient to 77 K
Rupture Strength	About 500,000 psi
Propellant Corrosion Resistance	No reaction with N ₂ O ₄ , ClF ₃ , or N ₂ H ₄ *

*Data provided by Astronautics Laboratory (AFSC).

3.3.3 Recent Properties Data Measured on Other Contracts--Crystallume has just completed measurement of thermal conductivity and oxidation behavior of CVD diamond film for Air Force Weapons Research Development Center (AFWRDC).

Thermal Conductivity--Thermal conductivity of CVD diamond film has been measured under a Phase I SBIR contract from AFWRDC. The contract number is F33615-88-C-2859; report available for distribution 1 July 1989.

Thermal conductivity results are summarized in Figure 18 and Table 19, which show (a) thermal conductivity of CVD films, natural diamond, and copper as functions of temperature, and (b) thermal conductivity of several diamond films with synthesis conditions, (methane %, pressure), Raman peak width (FWHM), diamond/graphitic bonding ratio, and measured thermal conductivity at a specific measurement temperature. The major point of these data is that the thermal conductivity can be varied by changing methane concentration.

Oxidation--Under another Phase I SBIR from AFWRDC (Contract F33615-88-C-2852), the oxidation behavior of CVD diamond films was studied. Figure 19 and Table 20 show measured oxidation rates and activation energy for diamond films compared with natural diamond. In natural single crystals, there is a strong variation as a function of crystal orientation. The significant result is that CVD diamond oxidation rates are lower than the natural material. It may be that this is a simple orientation effect. The oxidation behavior of the films is quite complex.

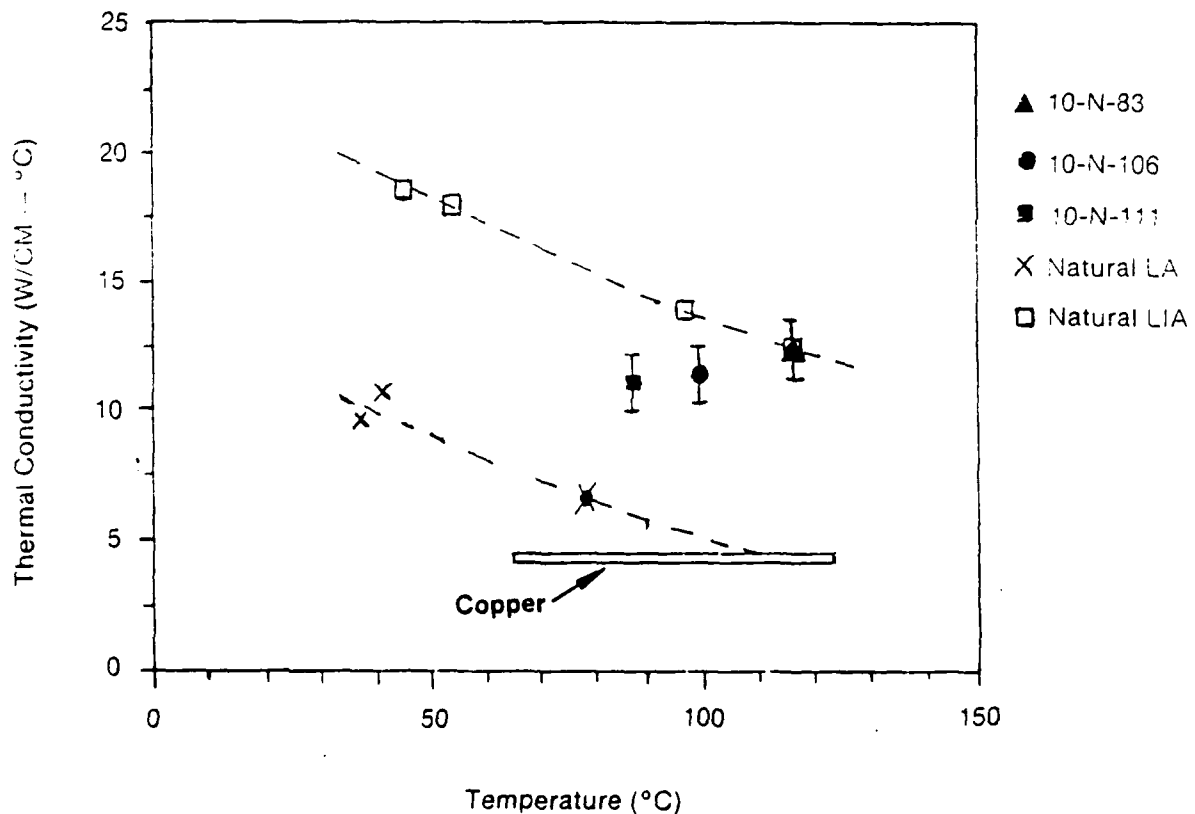


Figure 18. Thermal conductivity vs temperature for natural diamond and diamond films.

TABLE 19. Thermal Conductivity of Diamond Films

Deposition	Methane (%)	Pressure (Torr)	FWHM (cm ⁻¹)	Sp ³ /Sp ²	T.C. (W/cm ² C)	TM (°C)
Ila Nat. Diamond	-	-	3.3	-	14	100
10-N-106	1/0.05	50	4.6	22.7	11.3	99
10-N-83	0.1	50	6.9	20.3	12.3	117
10-N-111	0.1	50	7.4	20.6	11.0	86.9
10-N-107	0.3	50	10.9	3.3	5.6/5.4	89
6-A-35	2/2	22/45	10.4	2.4	5.3	70.3
1-Q-46	0.3	30	11.5	1.29	4.4	70
1-V-43	0.3	25	12.5	1.03	3.6/3.8	82
9-W-35	0.5	30	-	0.73	3	73.3

M10/DFT/Tab19.3-4

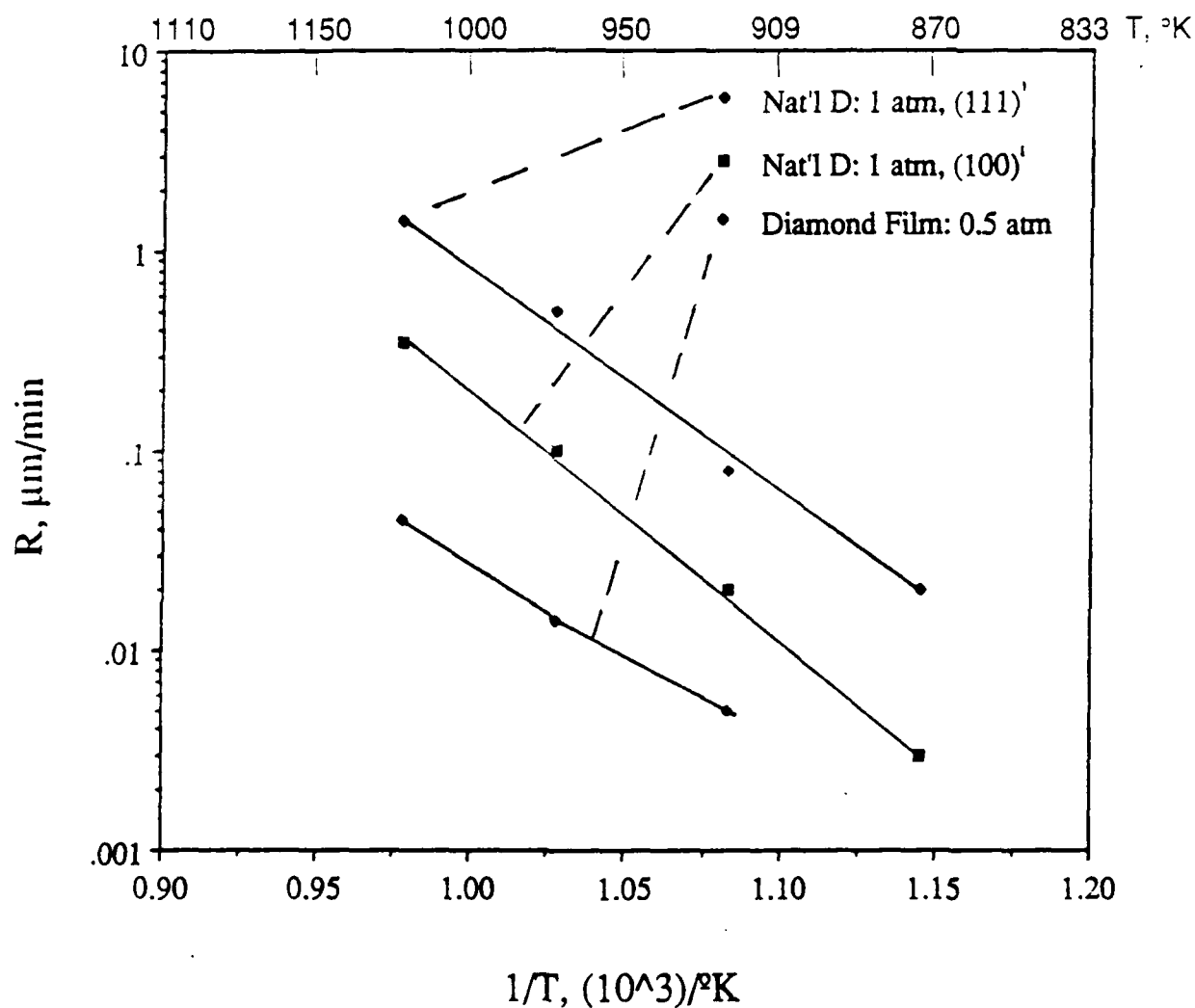


Figure 19. Arrhenius plot of diamond oxidation rates.

TABLE 20. Summary of the Oxidation Behavior of Natural and DC PECVD Diamond

	Natural Diamond	DC PECVD Diamond Film
Orientation	Strong Effect	Unknown
Graphite Formation	(110, (111)	All Films
Minimum T	600°C	600°C
Activation Energy, kJ/mole	~230	~ 170
Oxidation Rate, $\mu\text{m/hr}$	0.003 – 0.3	0.001 – 0.04

M7/DF/Tab1e3.3-5

3.4 OTHER SOURCES OF DIAMOND FILM TECHNOLOGY STATUS INFORMATION

In the process of conducting this study, data on recent and ongoing studies of diamond films and related materials were identified. Each study has its own emphasis and should be a good data source for that purpose.

The other surveys include:

(1) *Future Technology Survey, Inc. - No. 14: Diamond Films.* This is a privately funded report completed in the summer of 1988. Available for purchase from Ref. 6.

(2) *Gorham Advanced Materials Institute - Diamond and Diamond-Like Carbon Coatings Study.* This is in process, to be complete September 1989. Available for purchase from Ref. 8.

(3) *NASA/LeRC - Diamond Film Technology Transfer Study.* This is a one-year study which has just begun.

(4) *National Materials Advisory Board - Superhard Materials Study.* This study has been completed, is in the approval stage, and will be issued in the spring of 1989. Contact Dr. Joseph R. Lane, Senior Program Officer, NMAB, National Research Council, 2101 Constitution Ave., Washington, DC 20418.

(5) *Technical Insights, Inc. - Diamond Films: Evaluating the Technology and Opportunities.* This is a privately funded report issued in 1987. Available for purchase from Ref. 6.

Penn State Diamond Film Consortium--In addition, the Diamond Film Consortium, sponsored by Penn State University, consists of groups active in diamond synthesis who have access to recent developments in the field and improved contact with university researchers. One of the benefits of membership is access to an extensive bibliography of report and patent literature.

Recent Government Programs--Some government-funded activities in the diamond synthesis field are listed in Table 21. Recent DoD-solicited SBIRs potentially relating to diamond film synthesis and applications are listed in Table 22.

TABLE 21. Government Diamond Film Research Contracts

Sponsor	Contractor	Project Description	Sponsoring Location
Air Force	Crystallume	Recyclable UV Photoswitch	Air Force Armament Division
Air Force	Crystallume	Films for UV Instrumentation	Air Force Office of Scientific Research
Air Force	Crystallume	Oxidation Resistant Diamond Films	Air Force Wright Aeronautics Lab
Air Force	Crystallume	High Temperature Electronics	Air Force Wright Aeronautics Lab
Air Force	Crystallume	Diamond Plasma Thermochemistry	Air Force Office of Scientific Research
Air Force	Aerojet	Propulsion Applications Review	Air Force Astronautics Lab
Army	Crystallume	Diamond on GaAs	Army Strategic Defense Command
Army	Crystallume	Solid State Tunable Lasers	Army Night Vision and E-O Lab
DARPA	Hughes	Diamond Tribological Properties	DARPA
DNA	Crystallume	Alpha Particle Sensor Coating	Defense Nuclear Agency
DOE	Crystallume	Electronic Properties	Lawrence Livermore National Lab
DOE	DMI	Charge Neutralization Failures	
NASA	Crystallume	UV Detectors	Goddard Space Flight Center
Navy	Crystallume	X-Ray Lithography Mask Membranes	Naval Research Lab
SDIO	Crystallume	Diamond Materials Properties	SDIO/Office of Naval Research
SDIO	Crystallume	Silicon on Diamond Structures	SDIO/Office of Naval Research

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TABLE 22. DoD Diamond-Related SBIR RFP

Sponsor	Contract No.	Project Description	Sponsoring Location
Air Force	AF89-086	Complex Integrated Circuit Technology	AF Wright Aeronautics Lab
Air Force	AF89-122	High-Performance Carbon-Carbon Materials	AF Wright Aeronautics Lab
Air Force	AF89-136	Materials/Laser Interactions	AF Wright Aeronautics Lab
Air Force	AF89-139	Space Power -- Photovoltaics	AF Wright Aeronautics Lab
Air Force	AF89-143	Thermionic Energy Conversion	AF Wright Aeronautics Lab
Air Force	AF89-122	High Temperature Composites	AF Wright Aeronautics Lab
Air Force	AF89-139(2)	Space Power -- Power Device Cooling	AF Wright Aeronautics Lab
Air Force	AF89-124	High Performance Light Metal Alloys	AF Wright Aeronautics Lab
Air Force	AF90-123	High Temperature Materials	AF Wright Aeronautics Lab
Air Force	AF89-187	Survivable Space Power	AF Astronautics Lab
Air Force	AF89-219	Radiation-hard Semiconductors	AF BMO, Norton AFB
Air Force	AF89-027	Corrosion-Resistant Pressure Transducers	Arnold Engineering Dev. Center
SDIO	SDIO-013	Structural Materials	SDIO/AFWAL
SDIO	SDIO-006	Nonnuclear Space Power	SDIO
SDIO	SDIO-014	Electronic Materials	SDIO
Navy	N89-095	Integral Dielectric Heat Sinks	Naval Sea Systems Command
DNA	DNA-006	Directed Energy Effects	Defense Nuclear Agency

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4.0 AEROSPACE APPLICATIONS

Aerospace applications include subsets of commercial applications and unique uses which occur almost exclusively in space or noncommercial propulsion. After review of the diamond film literature, tabulation of the wide range of applications which have been suggested for diamond film, and brainstorming for advanced requirements, a matrix of aerospace applications was developed.

4.1 COMMERCIAL APPLICATIONS

Figure 20 is a chart which relates a dozen of diamond's properties to specific products in five classes of products: (1) tooling, (2) electronic substrates and heat sinks, (3) semiconductor devices, (4) optical and electro-optic material, and (5) high-performance structural materials.

A few applications are in production and development. Some of these, with the group conducting the activity and its status, are summarized in Table 23.

Cutting tools are being pursued by a number of groups. Figure 21 shows a diamond-coated drill bit for use in gang-drilling of electronic circuit boards. A surgical needle before and after coating with diamond film is shown in Figure 22.

Diamond has potential application in electronics in both passive and active elements. Seven classes of applications are shown in Table 24.

4.2 AEROSPACE APPLICATION MATRIX

A matrix was prepared to relate diamond properties to potential aerospace applications. Twenty-six of the properties of diamond film were chosen as being discriminators in one or more of the applications. To aid in classification, the applications were categorized into space vehicles, aircraft, missiles, and, as a separate classification, propulsion. The latter was further subdivided into chemical, electrical, and nuclear.

Each classification was further subdivided into major subsystem, subsystem, and component. At the final level, the list was limited to the more significant applications of diamond as opposed to "making everything with diamond."

The resulting matrix is shown in Table 25. It contains about 200 specific aerospace applications of diamond film which are potentially of major significance. The relative importance of each of the 26 properties to the application is rated, "high," "medium," "low," or "not applicable."

A summary of aerospace applications, which is a subset of the matrix, is shown in Table 26. This table was prepared to assist in screening applications. It shows probable application time frame and uncertainties which must be resolved to make the technology practical. Applications with long time frames and extensive uncertainties are less attractive for near-term technology demonstration.

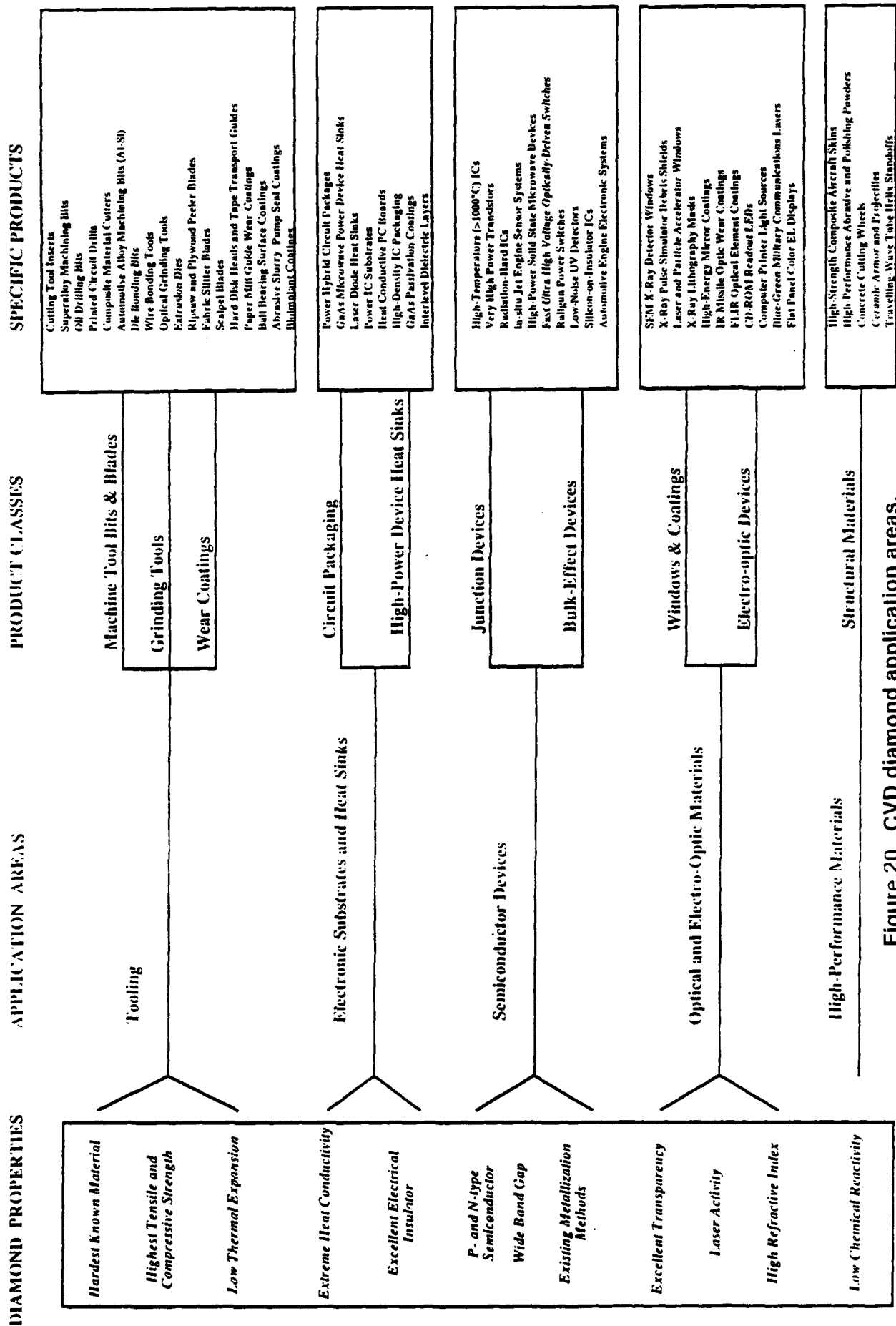


Figure 20. CVD diamond application areas.

TABLE 23. Diamond Film Production and Development Activity

<u>USE</u>	<u>BY</u>	<u>STATUS</u>
AUTOMOTIVE TURBOCHARGER BEARINGS	TOYOTA	DEVELOPMENT
CUTTING TOOL COATINGS	SEVERAL	DEVELOPMENT/ PRODUCTION
DRILL COATINGS	SEVERAL	DEVELOPMENT/ PRODUCTION
HIGH-TEMPERATURE SENSORS	SUMITOMO	PRODUCTION
HIGH-TEMPERATURE TRANSISTORS	DMI	DEVELOPMENT
HYPERSONIC AIRCRAFT LEADING EDGES	DMI	CONCEPTUAL
INTEGRATED CIRCUIT INSULATORS/HEAT SINK	SUMITOMO	PRODUCTION
LOUDSPEAKER	SUMITOMO	PRODUCTION
MAGNETIC DISK WEAR COATING	-	DEVELOPMENT
X-RAY WINDOW	CRYSTALLUME	PRODUCTION

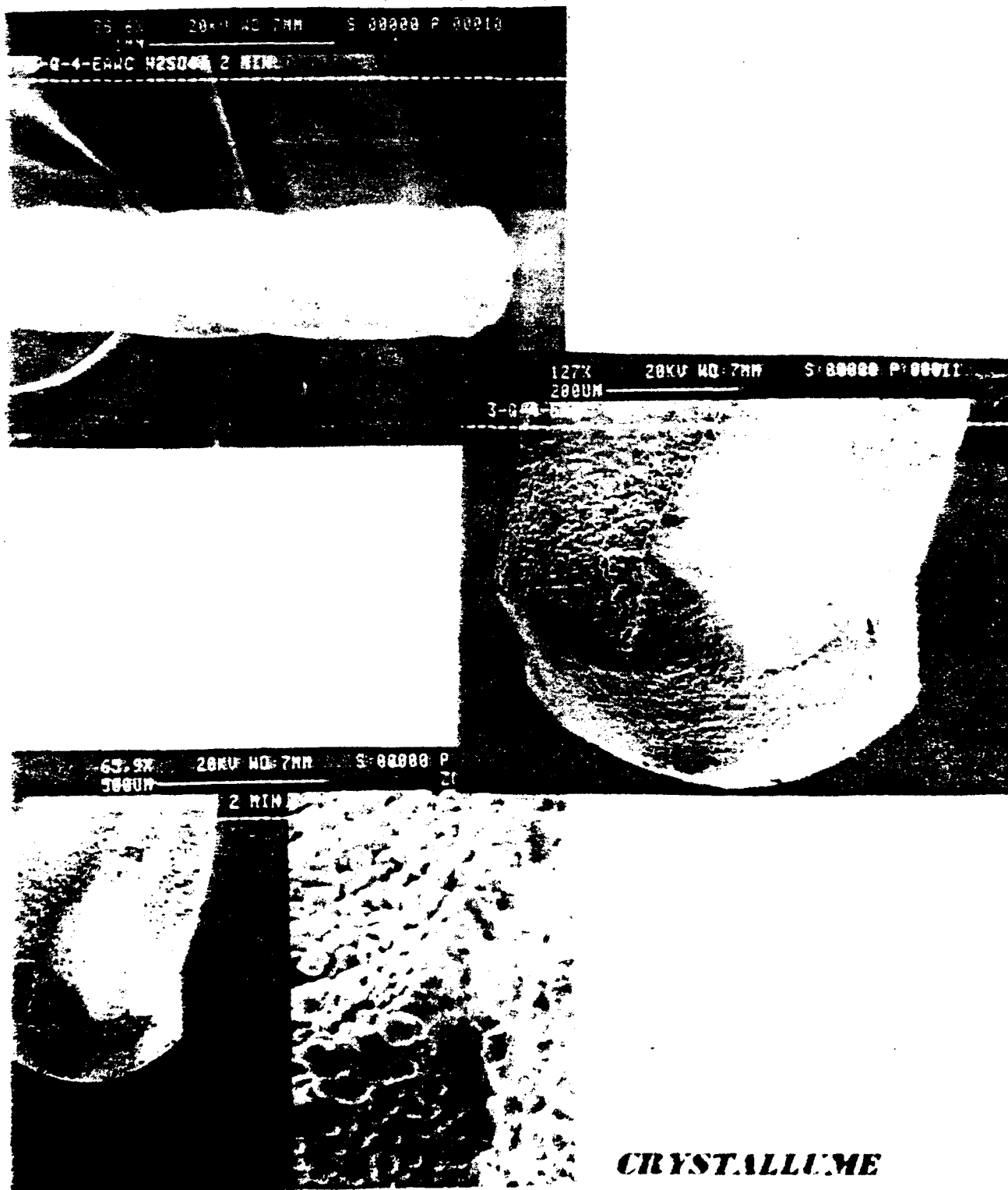
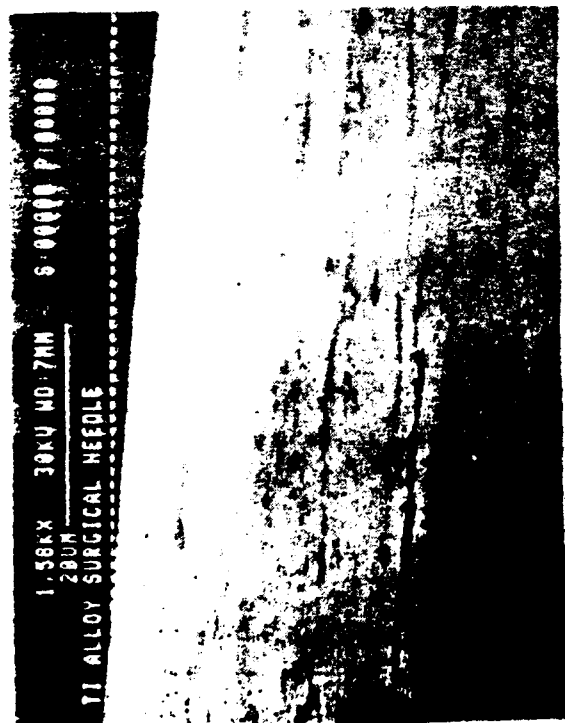


Figure 21. Diamond film deposited on a drill bit.



Prior to Diamond Deposition



Post Deposition

CRYSTALLINE

Figure 22. Diamond deposition on titanium surgical needle.

TABLE 24. Diamond in Electronics

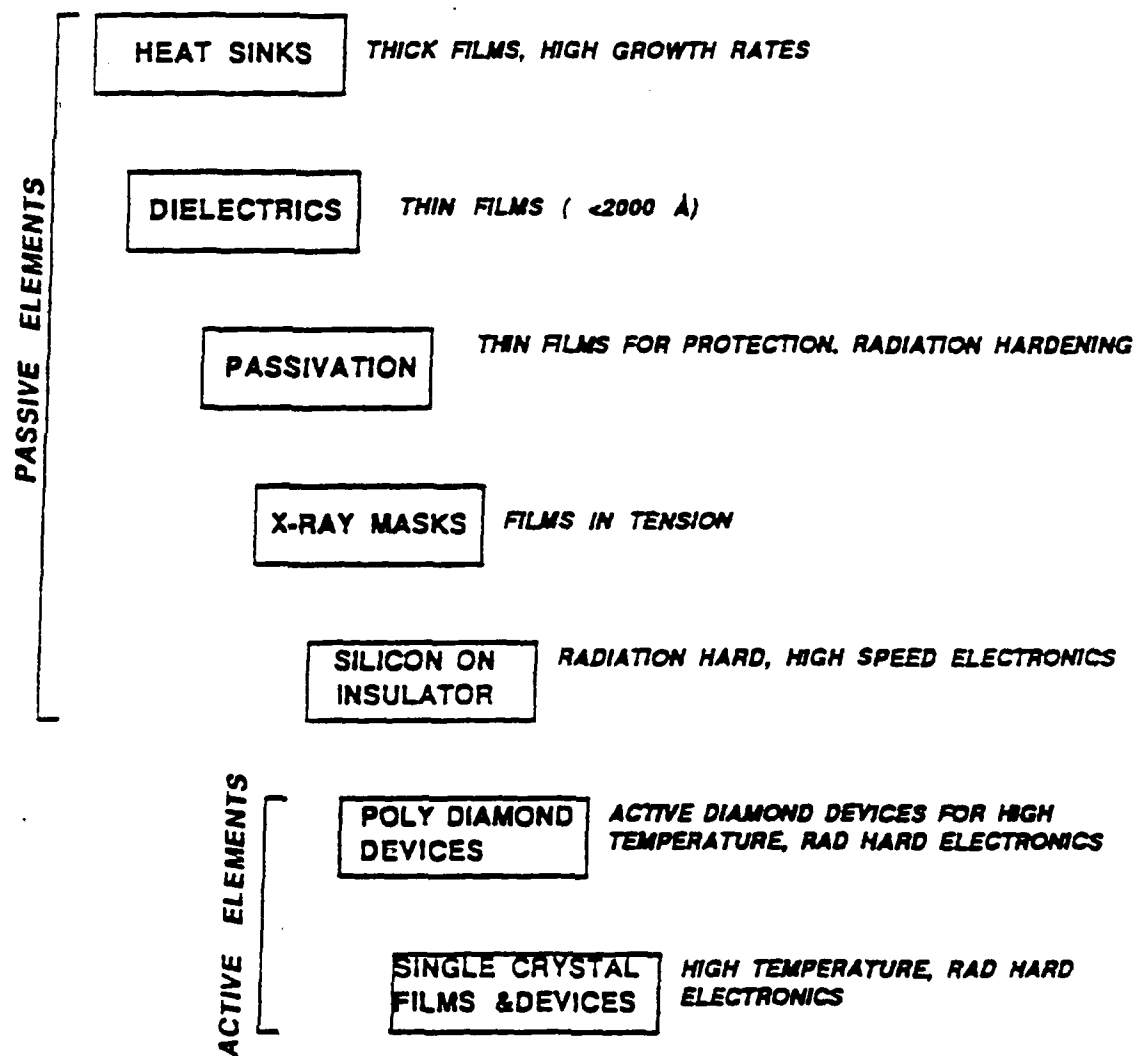


TABLE 25. Diamond Film Properties and Applications Matrix, Page 2 of 5

		ELECTRONIC										MECHANICAL										OPTICAL										THERMAL									
TYPE OF APPLICATION	MAJOR SYSTEM	SUBSYSTEM	COMPONENT APPLICATION	PARAMETER REPORTS																																					
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26												
Chemical Propulsion	Liquid	Turbopump Assembly	Bearings, seals	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Gears	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Turbine blades	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Impeller	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Gas generator duct	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
		Thrust chamber	Optical monitor	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Injector	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Throat	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Nozzle exit	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M				
			Valves and Controls	Seals, shafts & pintles	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M			
Electronics	M	M		M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Sensors	M	M		M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Optical transmission	M	M		M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Isolator	M	M		M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Structure Controls	Electronics	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
	Sensors	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
	Hot gas valve	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
	Composit case	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
	Nozzle	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Motor	Insulation	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
	Fairings	L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
		L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
		L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
		L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
Hybrid	(Same as Liquid + Solid)		L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						
			L	L	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M						

TABLE 25 Diamond Film Properties and Applications Matrix, Page 4 of 5

			ELECTRONIC										MECHANICAL										OPTICAL										THERMAL																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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TABLE 26. Significant Applications of Diamond Film to Propulsion

Application	Benefit To	Estimated Benefit Level	Application Time Frame	Uncertainties
Hypersonic Leading Edges	Aerospace Plane	Medium	5-10 yr	- o Can it operate below its oxidation temperature? - o Can it withstand thermal cycling?
Bearing Surfaces	ALS, OTV, XLR-132	High	Immediate	o Can it withstand cyclic loading?
Valve Seats and Pintles	Metallized Propellants	Medium	Immediate	o Can it withstand cyclic loading?
Corrosion-Resistant Coatings	Corrosive Propellants	Medium	Mid-Term	o Coating adhesion, imperfections, chemical compatibility.
Electrically Insulating Thermal Shunts	Electric Propulsion	Medium	Mid-Term	o Adhesion, interface thermal resistance, thermal cycling.
Microwave Power Transistors	Electric Propulsion	High	Mid-Term	o Electronic compatibility as insulator replacement and as semiconductor replacement.
Power Capacitors	Electric Propulsion	High	Mid-Term	o Geometry mods to utilize high thermal conductivity; film failure.
Rad Hard Electronics	Nuclear Propulsion; DoD Space Missions	High	Mid-Term	o Electronic compatibility as insulator Replacement and as semiconductor Replacement.
Nuclear Light Bulb Chamber	Nuclear Propulsion	High	20 yr	o Radiation effects on bulk optical properties; capability to produce diamond structure.
First Wall-Fusion Reactor	Nuclear Propulsion	High	10-20 yr	o Radiation effects on bulk properties; capability to produce diamond structure.
Laser Thruster Optics	Laser Propulsion	Medium	Mid-Term	o Effects of high intensity optical radiation on optical properties.
Microwave/RF Thruster Chamber	Electric Propulsion	High	Mid-Term	o Thermal design to maintain dielectric properties; capability to produce diamond structure.
Fiber Composite Structures	Aerospace Structures	High	Immediate	o Capability to coat compatible substrate fiber; development of tensile strength high enough to justify replacement of graphite fibers.

To reduce the number of applications to a manageable list, benefit assessments were made, first by generic application. Table 27 is an assessment of the potential benefit of an application by system and vehicle type. As might be expected, the applications with high benefit potential are those for high-value vehicles.

The applications which show the highest quantifiable potential benefit are those in which use of diamond can prevent catastrophic failure. Table 28 assesses these protective applications for specific aerospace systems. The value of the diamond in the application is computed in terms of the failure avoidance savings.

Five applications of diamond film were assessed to be of high potential for Air Force aerospace uses, and which warranted further consideration for near-term technology development. These applications were: (1) bearing surfaces, (2) hydrogen barriers, (3) monolithic structures, (4) composite structures, and (5) thermal protection. Table 29 lists specific Air Force uses and potential benefits.

Further consideration of these potential applications included properties characterization measurements. These measurements, discussed in Section 5, served to determine if the characteristic necessary for the advanced applications could probably be achieved with CVD diamond.

In addition, brief analyses were made to attempt to quantify the applications' technical potential in more detail. These analyses are discussed below, along with discussion of several other applications which are more generic in nature. These latter applications have sufficient commercial utility that they will be developed without the need for Air Force funding.

4.3 PRELIMINARY APPLICATION ANALYSIS

Scoping evaluation was made of several suggested applications which have utility for specialized uses. This work is summarized here.

4.3.1 Thermal Protection--Diamond film is suitable for protecting surfaces from high, nonuniform heat flux by reducing peak surface temperature. Figure 23 illustrates its ability to reduce surface temperature for a specific example: a nickel surface exposed to $10 \text{ Btu in.}^{-2} \text{ sec}^{-1}$. Note that a 0.1 mm (0.004 in.) thick layer with 20% of the surface heated can reduce the peak temperature by 260 C (500 F). This is a significant reduction for materials which are being pushed to their design limits.

Table 30 lists some potential applications for thermal protection. Key to the ability of diamond film to reduce the temperature is (1) diamond's very high thermal conductivity and (2) a surface which is heated only locally.

4.3.2 Composites Using Diamond Films and Fibers--Study of structural applications of diamond was triggered by reports of tensile strength in the 3 million psi range, since this is well above the tensile strengths available in existing engineering materials. T-1000 carbon fiber, for example, used in filament-wound structures, has a tensile strength of 1.3 million psi. Since the most likely tensile strength of diamond is 500,000 psi, it is not competitive with graphite fibers. Because of its availability as a film, diamond still could be practical for laminated structure applications.

TABLE 27. Benefit Assessment Criteria by Vehicle System

SYSTEM TYPE	VEHICLE TYPE	EQUIPMENT COST	PERSONNEL EXPOSURE	MISSION CRITICALITY	REDUNDANCY	BENEFIT POTENTIAL
Aircraft	Trainer	low	med	low	high	low
	Fighter	med	med	med	high	med
	Tanker/transport	med	high	med	med	med
	Bomber	very high	high	high	low	med
Missiles	Manned hypersonic	very high	med	high	low	high
	Air to air	low	low	med	high	low
	Air to ground	low	low	low	high	low
	Ground to air	low	low	med	high	low
	Ground to ground	high	med	high	low	med
Satellites	Space launch system	high	med	med	med	high
	Command, cont. & comm.	med	--	high	med	med
	Surveillance	med	--	high	med	med
	Ballistic missile defence	high	--	high	med	high
	Manned station	very high	high	high	low	high

TABLE 28. Diamond Film Value in Aerospace Applications

DIAMOND FILM VALUE IN AIR FORCE APPLICATIONS

APPLICATION	BASIS	GRAMS DF/ UNIT	FAILURE AVOIDANCE SAVINGS	BASIS	ROM VALUE OF DF. \$/GRAM
Space shuttle†	Bearing surfaces	600	\$3 B	Shuttle replacement	\$5 M/gm
"	Impeller surfaces	4000	\$3 B	Shuttle replacement	\$ 0.8 M/gm
Adv. Launch Vehicle	Bearing surfaces	500	\$1 B	Payload replacement	\$2 M/gm
Surveillance sat.	Impact armor	35,000	\$1.5 B	Satellite replacement	\$40,000/gm
B-2 Bomber	Impact armor	500,000	\$0.5 B	Vehicle replacement	\$1000/gm
Fighter (F-16)	Bearing surfaces	500	\$20 M	Vehicle replacement	\$40,000/gm
Hypervelocity vehicle	Leading edges, inlets	100,000	\$5 B	Vehicle replacement	\$50,000/gm

†Shown for reference

TABLE 29. Potential Air Force Applications of Recommended Diamond Film Technology Development

Application	Specific AF System Uses	Benefit Summary
Bearing Surface	ALS TPA	Increased life, reduced development and operating costs
	XLR-132 TPA	Increased life
	XLR-134 TPA	Increased Life
Hydrogen Barrier	ALS Engine	Increased life, reduced development and operating costs
	B-1 Bomber Titanium	Increased life
	XLR-134	Increased life
Monolithic Structure	Propellant Tanks	Alternate fabrication technique with performance growth potential
	Helium Tanks	Greatly reduced mass
Composite Structure	ALS	Reduced system cost, increased performance
	Hypersonic Vehicle	Potentially enabling
	Satellite Protection	Potentially enabling
Thermal Protection	ALS	Increased life, reduced cost
	Hypersonic Vehicle	Potential enabling

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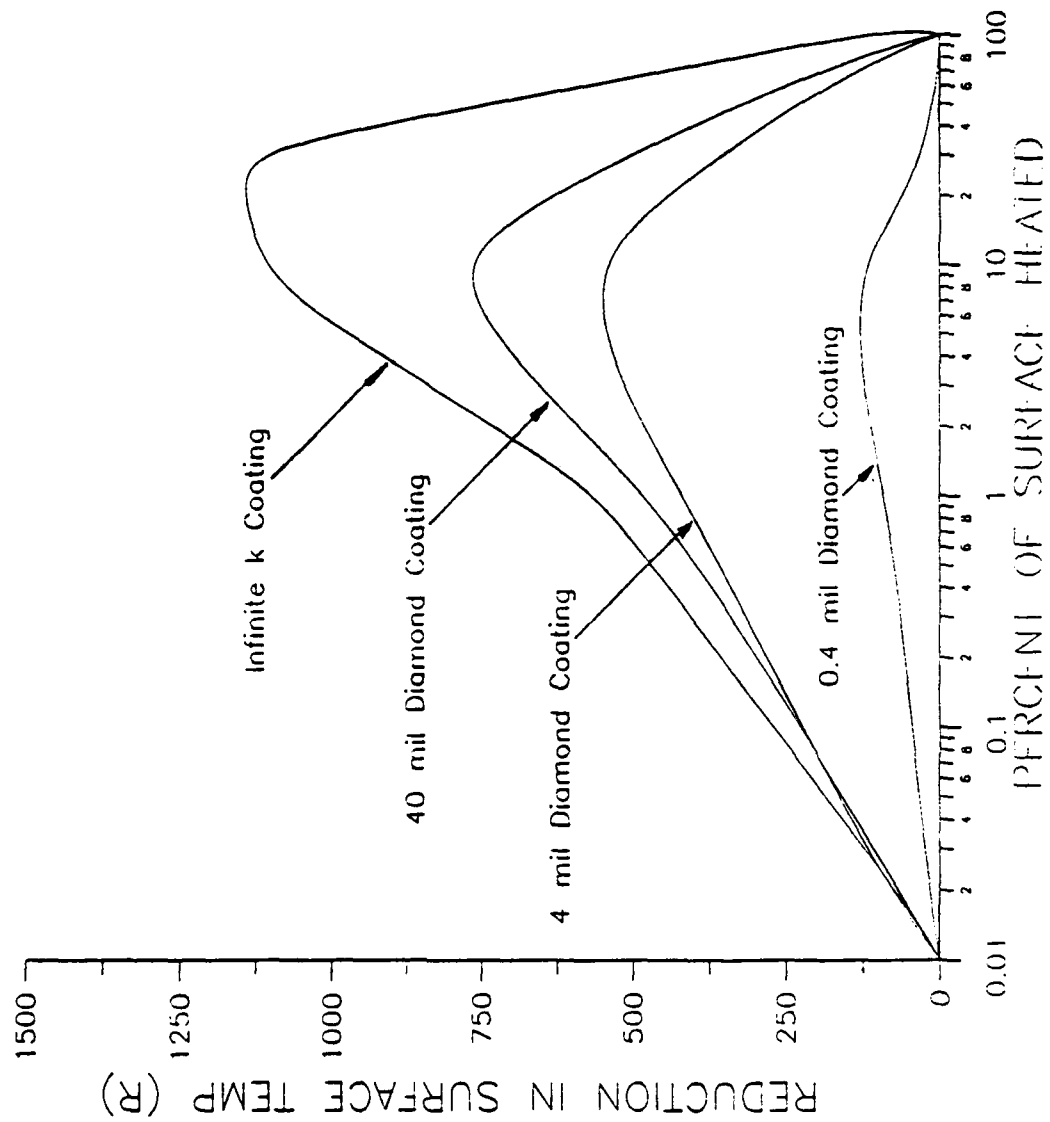


Figure 23. Peak surface temperature reduction by diamond film.

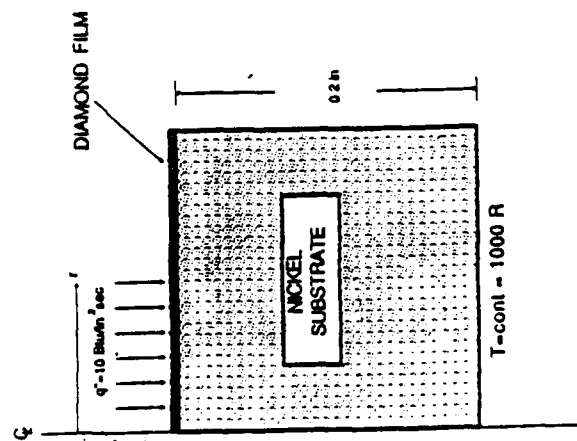


TABLE 30. Thermal Protection Coating Applications

PRIMARY APPLICATION

- o **REDUCTION OF PEAK TEMPERATURES IN NONUNIFORM, HIGH HEAT FLUX APPLICATIONS**

POTENTIAL AIR FORCE USES

- o **LEADING EDGES, INLETS, AND FUEL STRUTS OF HYPERSONIC AIRCRAFT**
- o **TURBINE AND STATOR BLADE COATINGS IN FUEL-RICH GAS GENERATOR ROCKET PROPULSION CYCLES**
- o **NOZZLE ENTRANCE AND INJECTOR FACE THERMAL PROTECTION COATINGS**

All composites are comprised of at least two constituents, the matrix and the reinforcement(s). Before composites reinforced with diamond can be discussed, a classification scheme is needed. One simple composite classification scheme is to separate them according to their reinforcement form; particulate, laminar, and fiber. Particulate-reinforced composites are defined as those that have reinforcements with roughly equal dimensions, e.g., spheres, cylinders, rods, etc. Laminar-reinforced composites are those composed of two or more layers with two of their dimensions much greater than the third. Fiber-reinforced composites are separated into two categories, discontinuous and continuous. Discontinuous reinforcements are those that, when increased in length, will change the properties of the composite, whereas continuous reinforcements are those that do not affect the properties if the fiber length is increased. The composites' properties, mechanical, physical, electrical, optical, etc., are to a large extent dictated by the properties of the reinforcement.

If one were to consider the reinforcement constituent to be fabricated from diamond, either film or fiber, then, because of the widely different properties of this material, the possibility to produce composites with different characteristics exists. This report briefly compares and contrasts the properties of diamond to existing reinforcements, discusses potential benefits, assesses candidate matrix materials, and predicts properties. Since diamonds are produced by deposition techniques, it seems reasonable to assume the primary forms will be as either a thin film over a fiber or as a flat thin film which could be used to produce a laminar-type composite. Therefore, the discussion below is focused on fiber-reinforced composites and laminar composites.

Fiber Reinforcement Composites--In this section, the properties of some typical fiber reinforcements are presented and compared to the properties of diamond. For convenience, this section is separated into two subsections, discontinuous and continuous reinforcements.

Discontinuous: Discontinuous reinforcements can be chopped fibers, whiskers, or particulates, and are generally ceramic or carbon. Table 31 has been prepared to show some typical properties of discontinuous fibers.

TABLE 31. Characteristics of Discontinuous Fibers

<u>Material</u>	<u>Diameter</u> <u>μm</u>	<u>Density</u> <u>g/cc</u>	<u>UTS</u> <u>ksi</u>	<u>E</u> <u>10^6 psi</u>	<u>CTE</u> <u>$10^6/\text{C}$</u>
SiC	0.2	3.2	120	75	4.3
SiC	120	3.2	-	-	-
Al_2O_3	3	3.3	290	45	8.1
Mullite	3	3.2	100	20	5.1
Aluminosilicate	2	2.7	250	15	-
Zirconia	5	5.7	-	30	10.5
Carbon (PAN)	7	1.8	480-350	30-55	-0.6
Diamond	TBD	3.5	500	150	0.8

These types of reinforcements are generally used in either metal matrix or ceramic matrix composites (MMC or CMC). Their use in MMCs is primarily to increase specific strength or specific stiffness. Some typical tensile data for a reinforced aluminum alloy are presented in Figures 24 and 25. As can be seen, as fiber volume is increased from 0 to 20 volume percent, the mechanical properties tend to increase. It should be noted that there is generally a corresponding decrease in fracture toughness of MMCs with increasing fiber volume content.

Based on the mechanical properties presented in the figures, it appears that both specific strength and stiffness would be improved using a diamond-coated fiber as the reinforcement. The issues associated with producing the composite would be the thermal expansion mismatch and the interfacial compatibility between the diamond fiber and its substrate and the selected matrix. These characteristics would dictate the mechanical properties of the composite, along with the thickness of the diamond film, the type of substrate (if any) and diamond-to-substrate bond strength, the fiber aspect ratio, the fiber volume, and the fabrication technique, e.g., powder metallurgy, casting, plasma spray, etc. Thus, to predict the change in mechanical properties based on a simple model, such as the rule of mixtures, is an oversimplification.

Mechanical properties for diamond composites were anchored to the SiC-reinforced data shown in Figures 24 and 25 by assuming that the SiC fibers were coated with diamond, resulting in a 25% increase in the fibers' properties. For a first-order approximation, an increase of 50% in the fiber properties (as determined using the rule of mixtures for the fiber) will result in a 25% increase in the composite. For example, using the ultimate tensile strength in Table 31, the fiber would be 84 volume percent SiC and 16 volume percent diamond or, if the 120 μm SiC fiber were used, then the diamond coating would be about μm thick (or 10 μm on the diameter). Similarly, to achieve a 50% increase in fiber modulus, a coating of about 25 μm would have to be applied to the SiC fiber. This is a reasonable thickness for a diamond film. If other considerations are ignored (which is not a reasonable assumption, but must be made to predict properties), then the curve shown in Figure 26 can be developed. Similar scenarios can be developed for different substrates.

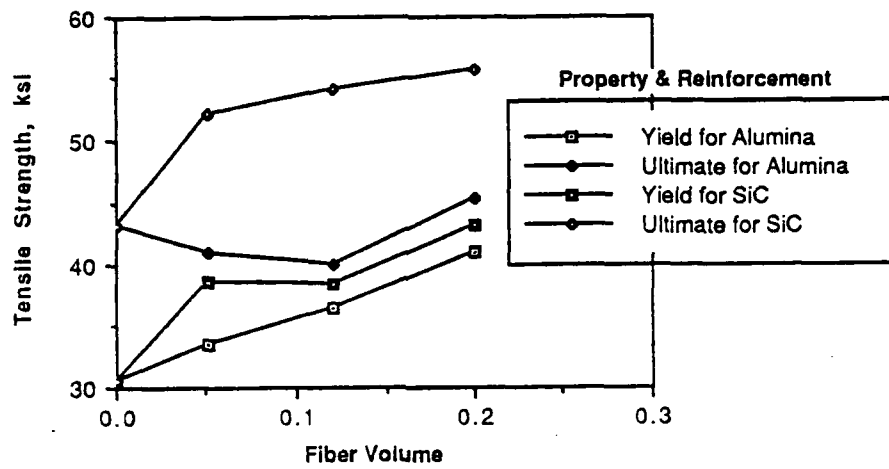


Figure 24. Tensile data on reinforced aluminum alloys.

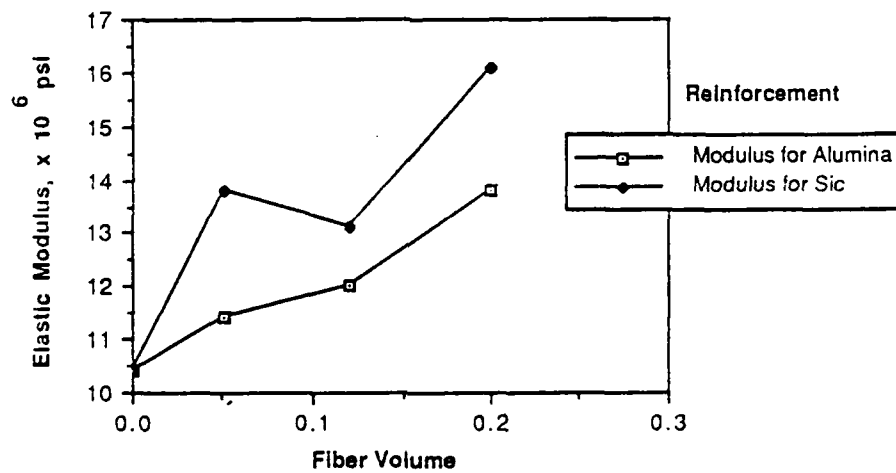


Figure 25. Elastic moduli for reinforced aluminum alloys.

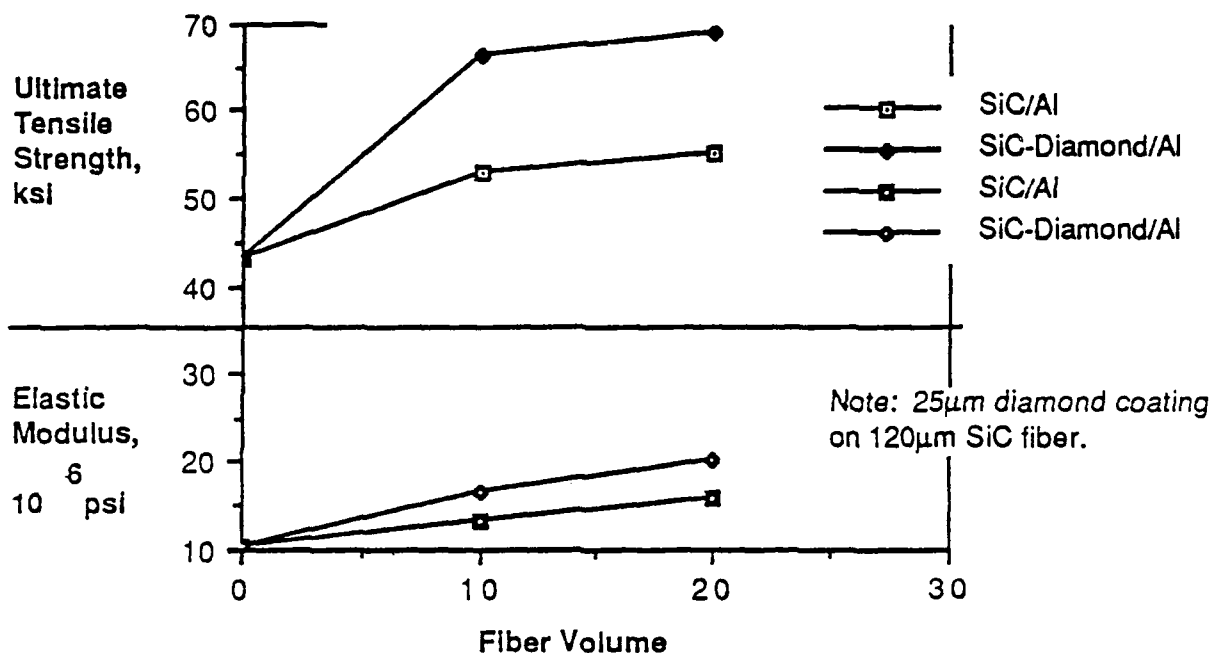


Figure 26. Projected properties for diamond film coated silicon carbide reinforced aluminum composite.

Discontinuous CMCs were developed primarily to increase the fracture toughness over the monolithic ceramic matrix, e.g., SiC whiskers have been added to a Si₃N₄ matrix to increase the fracture toughness of the Si₃N₄. Given the high specific strength and stiffness of the diamond, an increase in composites made with these types of fibers may dramatically improve both properties of the matrix. The same caveats that applied to MMCs would also apply to CMCs.

Continuous--Continuous fiber-reinforced composites yield the utmost in physical and mechanical properties because the properties of the composite are dictated primarily by the fibers contained therein. Therefore, if continuous diamond-coated fibers could be produced and made into a composite, one would expect significant improvements in properties produced with this type of reinforcement.

It seems reasonable to assume that continuous diamond fiber could be produced by depositing a thin diamond film over, perhaps, a carbon substrate. Therefore, the mechanical properties would be dictated primarily by the properties of the carbon fiber. However, because of the exceptional thermal conductivity of the diamond, one would expect a composite could be designed that would have extremely high thermal conductivity.

These composites could be produced in a manner similar to the fabrication approach used to produce continuous reinforced composites today. For example, diamond-coated carbon fibers could be wound or laid-up, the matrix plasma sprayed, and sheets of this composite bonded together. Issues similar to those discussed above are still relevant for continuous fiber-reinforced composites.

Organic matrix composites could also be produced using diamond-coated fibers. Again, the principal benefit would appear to be one that takes advantage of the physical properties of the diamond rather than the mechanical properties.

Laminar-Reinforced Composites--Laminar composites could be produced using diamond films which are individually made and stacked and bonded together, similar to plywood construction. It is expected that the properties in the plane of the composite would be the same and those in the short transverse direction would be different (not unlike rolled beryllium sheet). The weakest link would be the interlaminar shear strength of the composite. The composite could be comprised of layers made from different materials which would change the properties of the material. For instance, the thermal conductivity in the plane direction would be high while, in the short transverse direction, it could be much lower.

More work needs to be done to examine these types of composites. They could be used for pressure vessels, aerodynamic surfaces, impact protection, and high-performance structures. Their potential value is strongly dependent on the achievable UTS for CVD diamond. The value used here, 0.5 million, is based on natural diamond. Burst test data described in Section 5 give values up to 0.7 million, with an indication of possible increase with thickness. No attempt has been made to optimize CVD diamond tensile strength through process control.

The possible forms of the material are illustrated in Figure 27 for fiber composites, and Figure 28 for laminated composites. Figure 29 illustrates two possible techniques for fabrication of the film; one using conventional small-specimen, 10-cm wafer technology, and the other using large-surface technology. The latter would use a modification of existing plasma sputter coating in which films 1.5 meter wide by kilometers long are coated in a continuous process. Present production techniques permit depositing up to three different materials on a substrate layer of plastic or thin metal film.

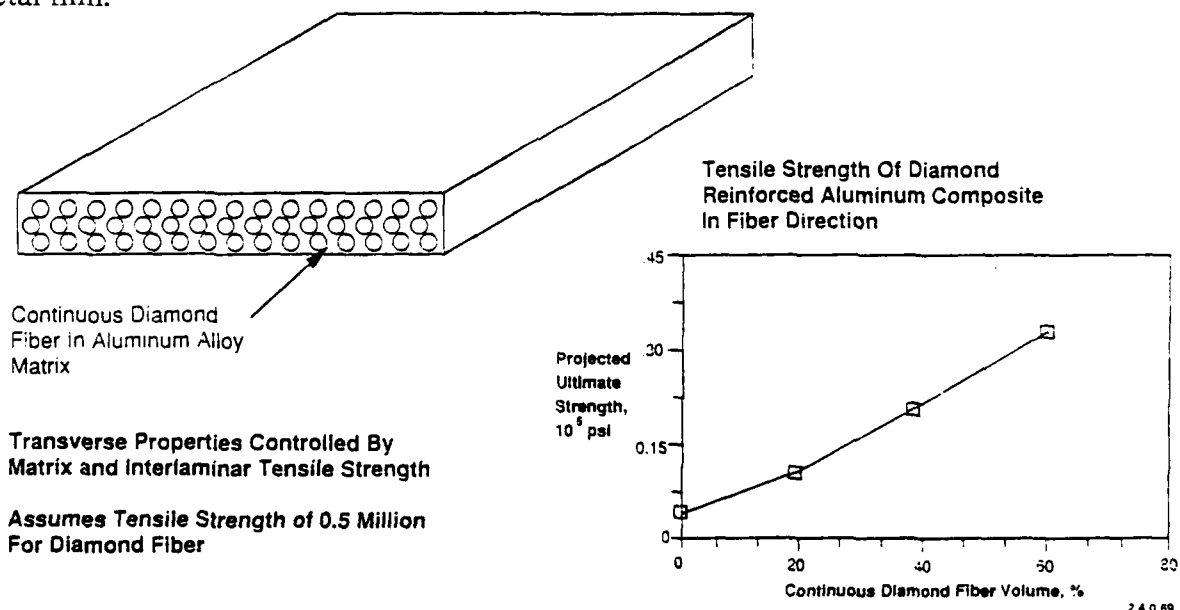
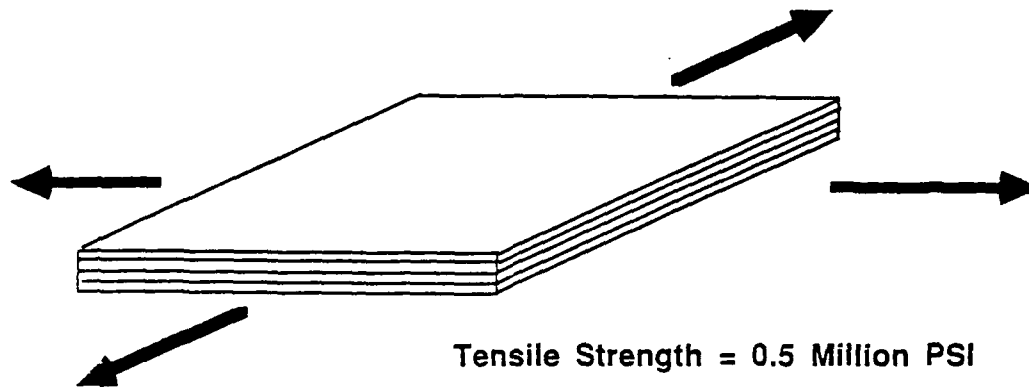


Figure 27. Continuous reinforced aluminum composites maximize properties in diamond film fiber direction.



"Plywood Construction"

Properties in Short Transverse Direction
Controlled By "Glue"

Figure 28. Diamond films laminated together offer high strength in planar direction.

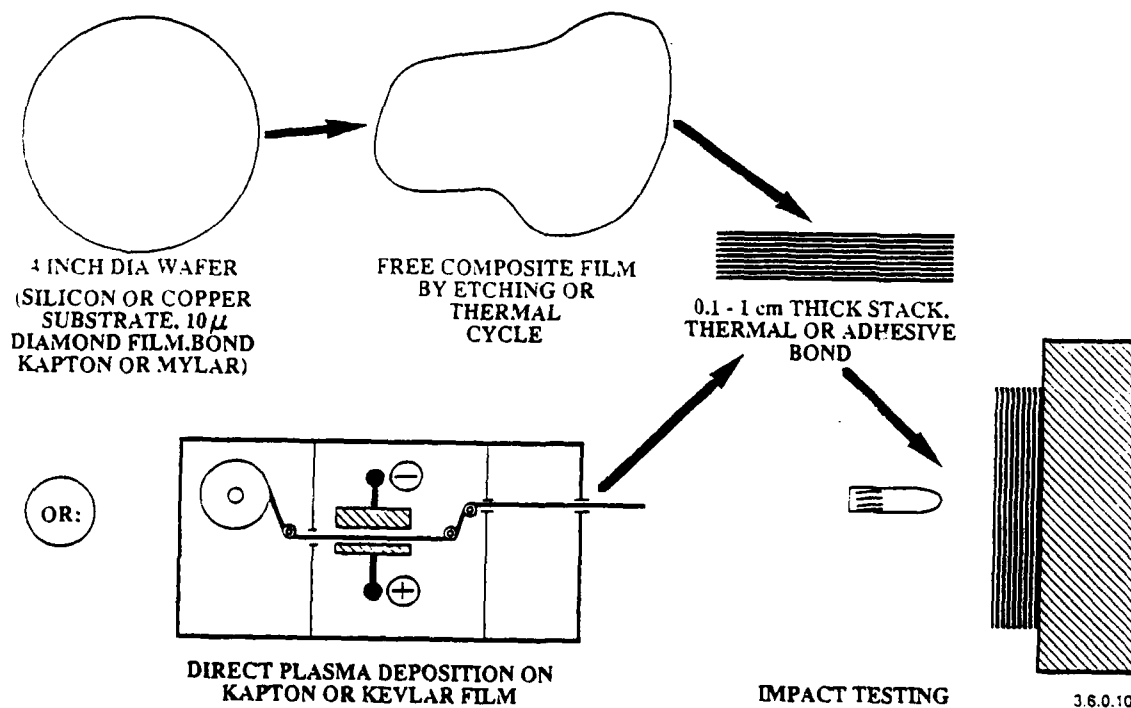


Figure 29. Impact armor concept.

Some of the impact armor applications include:

- o Micrometeoroid protection
- o Satellite battle protection
- o Aircraft armor
- o Body armor
- o Rain and dust impact protection in hypervelocity atmospheric flight

A typical laminate for this application is illustrated in Figure 30. It would use a Kevlar or Kapton substrate with a molybdenum interlayer to provide good adhesion for the CVD diamond layer. A thermal bonding layer would be applied to the substrate so that a thick laminate could be built up by stacking and vacuum thermal bonding, such as is done for Kapton flexible circuit bonds.

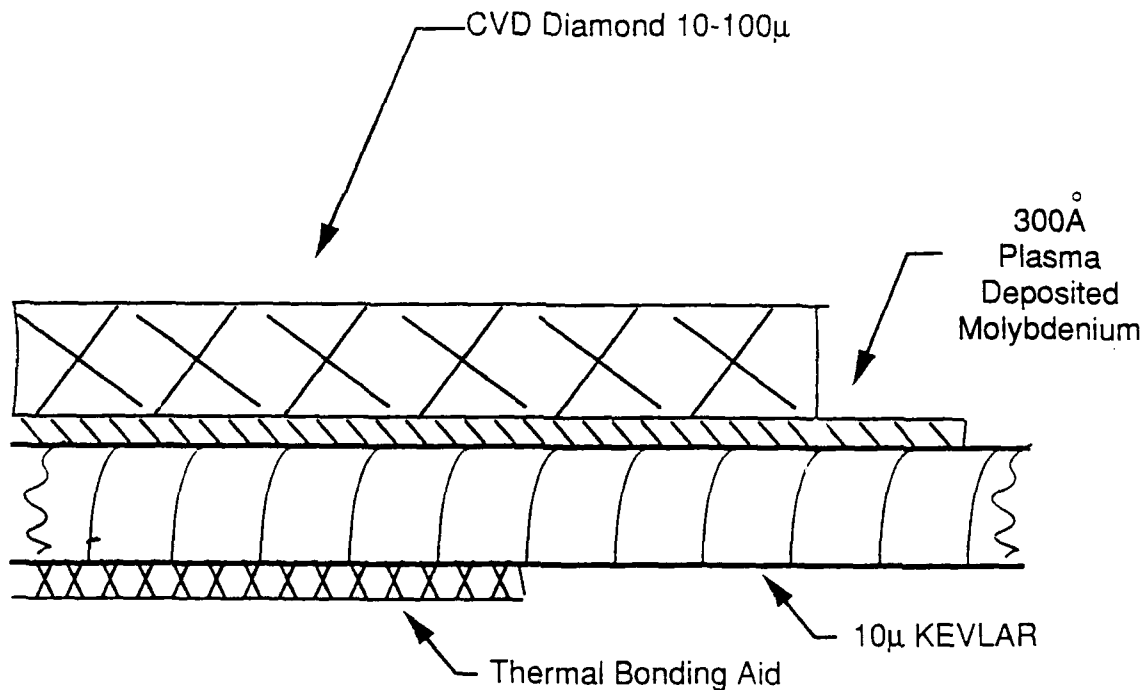


Figure 30. Single layer for laminate buildup.

Some of the design features which must be considered are:

- o Deposition process parameters
- o Diamond film thickness relative to substrate
- o Diamond film crystal structure
- o Diamond film purity
- o Composite optimization
- o Substrate material properties
- o Carbide-forming interlayer
- o Laminate adhesion layer

Laminates of such a material could be used against a range of impact threats:

- o Low velocity (e.g., typical aircraft intercept)
- o Medium velocity (e.g., hypervelocity intercept)
- o High velocity (e.g., orbital intercept)

4.3.3 Electronic Applications--Although the Air Force is a significant user of advanced electronics, activity directed toward development of such applications was considered to be generic in nature and off the main interest of this study of aerospace applications. However, information developed on some electronic applications is discussed here.

4.3.3.1 Electronics - Cooling--A passive electronic application for diamond film is in heat removal from electronic devices. Aerospace control, sensor data acquisition, storage, and transmission systems currently employ integrated circuits; their use is rapidly expanding for control, safety, and health monitoring applications. The life and reliability of integrated circuits are limiting factors in their application.

The life of integrated circuit devices is an Arrhenius function of the junction temperature. Reduction of the thermal resistance of the heat conduction path for cooling can reduce junction temperature at a given power level, thereby increasing life or permitting operation at higher power levels at a given life. Diamond has nine times the thermal conductivity and about ten times the dielectric strength of the next best thermally conductive electrical insulator, beryllium oxide. Figure 31 shows the effect of diamond on the temperature drop across a film at fixed flux compared to other materials in use. However, when diamond film is used as an external isolator to replace BeO, little reduction in junction temperature will be achieved since most of the thermal resistance is in the junction-to-case path. Therefore, realizing the benefits of diamond film requires integrating it into the fabrication of the semiconductor device to replace insulating layers such as sapphire (Al_2O_3) or SiO_2 . Design studies have shown the operating power of microwave transistors can be increased by more than a factor of two (Figure 32), providing smaller, lighter-weight space power conditioning.

4.3.3.2 High-Temperature Power Capacitors--Because of its high dielectric strength and high thermal conductivity, coupled with its capability to be fabricated into thin films, diamond can be used as an insulator for high-temperature capacitors. In addition to applications to integrated circuit devices, diamond films

appear to have application to power conditioning units (PCU) as well. PCUs are a major component of aerospace systems, in general, and electrical propulsion systems, in particular. To stay within reasonable mass limitations, PCUs must operate at high power densities. This reduces their conversion efficiency and makes them system life limiters.

Nearly all electrical propulsion applications require a PCU that interfaces the vehicle power source to the propulsion device. The major portion of a state-of-the-art PCU is a switching power supply, DC-DC for arc, ion, microwave, and MPD, and DC-AC for RF thrusters. The power, filter, and RFI isolation circuits require power capacitors that account for a significant fraction of the PCU mass. The life of these units is increased by a factor of two for every 10 C drop in operating temperature. Dielectric heating in high-frequency switching power supply capacitors generates internal heat that must be conducted to a heat sink. Poor thermal conductivity of plastic film insulators and their low operating temperatures limit capacitor power density and life. Use of tantalum metal film on diamond film construction would provide an increase in maximum internal operating temperature by a factor of three, insulator dielectric strength by a factor of six, and a decrease in overall thermal resistance by a factor of more than two. When configured to take advantage of the properties of diamond, tantalum-diamond capacitors, capacitors, Figure 33, should have nearly an order of magnitude size decrease relative to plastic film capacitors. Use of diamond-like carbon films in capacitor fabrication is described in Ref. 10.

4.3.3.3 Active Devices--If reliable techniques are developed for p- and n-doping of CVD diamond film, as well as for its epitaxial growth, it will be a semiconductor material superior to silicon and germanium arsenide and capable of

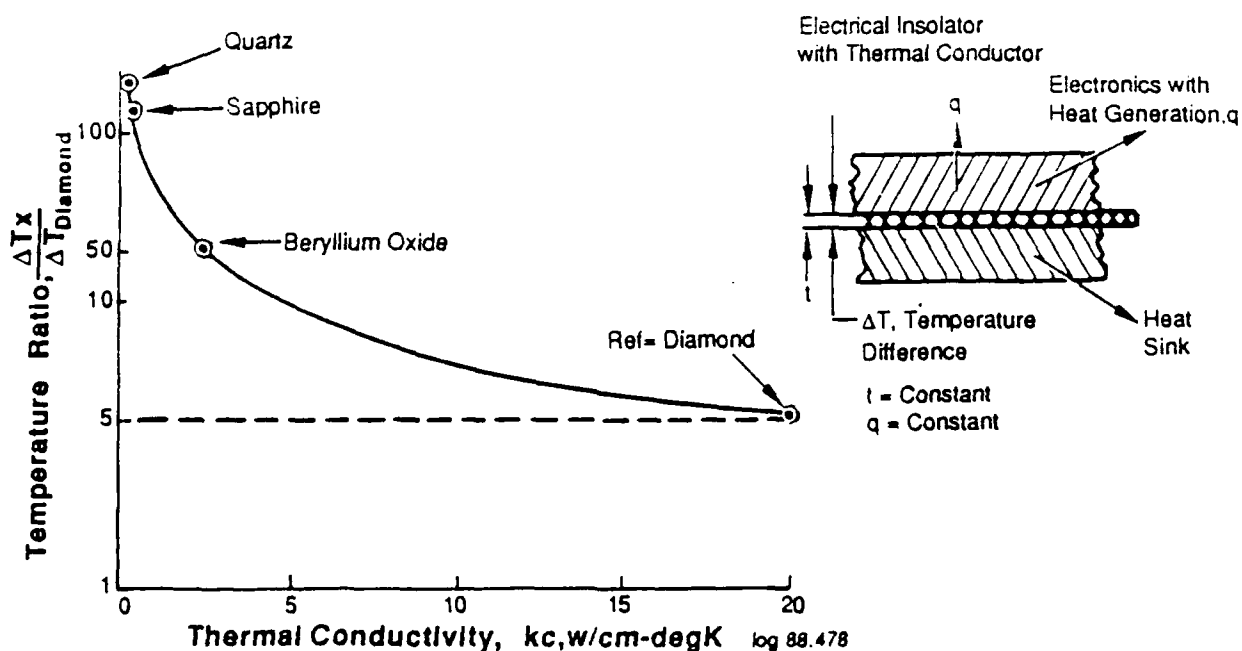


Figure 31. Electronics cooling through diamond film insulation compared to other electrical insulators.

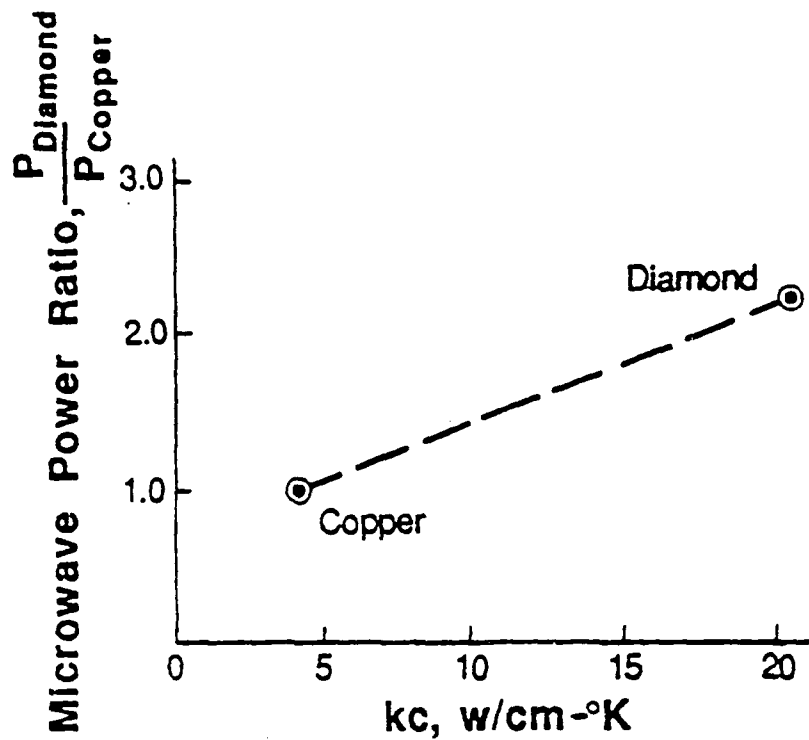


Figure 32. Semiconductor microwave generator dependence of power capability on heat sink thermal conductivity.

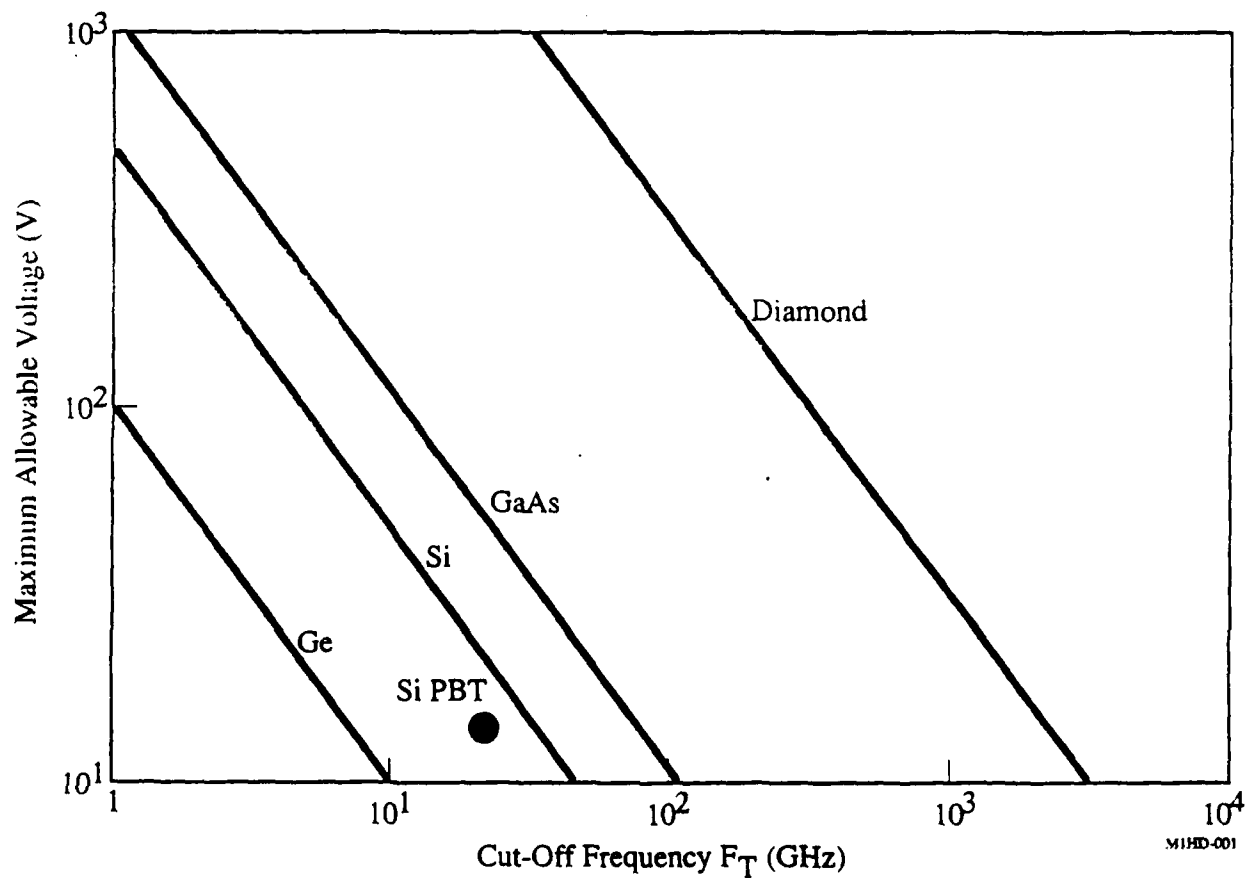


Figure 33. Fundamental device operation limits.

elevated temperature operation. Production of semiconductor-grade diamond is being developed (Refs. 11 and 12); recent reports of epitaxial growth of diamond film (Ref. 13) have been retracted (Ref. 14). Table 17 lists some pertinent electronic properties of diamond.

Diamond has exceptionally good characteristics for high-voltage, high-frequency devices such as microwave power diodes. Figure 33 from Ref. 15 compares the voltage frequency capability of diamond with conventional semiconductor materials.

4.3.4 Optical Applications--Activity is under way for DoD development of CVD diamond for IR windows for sensors and missiles (Ref. 16). Primary requirements for these applications are fine crystallite structures at least an order of magnitude smaller than the wavelength of interest and high purity with absence of graphite contamination.

4.3.5 Diffusion Barriers--As described in Section 5, preliminary experiments show that a thin film (4000 Å) of CVD diamond is impervious to helium and hydrogen. Table 32 lists some applications which can benefit from this characteristic. The most promising propulsion application is for hydrogen turbopumps in systems such as the Advanced Launch System (ALS), Space Shuttle Main Engine (SSME), and the XLR-134 space transfer engine. For high-performance hydrogen pumps, the material of choice for the impeller is a titanium alloy because of its high strength-to-density ratio. However, titanium alloys are attacked by hydrogen even at low temperature. Although the design limits for the titanium are not clear, it appears from recent work that, to be used successfully, it must be working below its elastic limit throughout the part, a difficult design feat for a complex, highly stressed shape such as an impeller. Until recently, it was believed that 70 ppm hydrogen concentration was acceptable in titanium alloys (Ref. 17). However, recent Air Force work shows hydrogen embrittlement of titanium alloy on the B-1 bomber hydraulic system at 10 ppm hydrogen (Ref. 18).

TABLE 32. Hydrogen Diffusion Barrier Applications

- ALS Hydrogen Pump
- XLR-134 Hydrogen Pump
- Hypersonic Aircraft Hydrogen Pump
- Fuel-Rich Gas Generators
- Hydrogen Storage Systems
- Fiberoptics Coatings

A related application is protection of fiber optic transmission cable from hydrogen contamination. Hydrogen diffuses very easily into the glasses used for low-loss optical transmission. Figure 34 from Ref. 19 shows the effect of hydrogen on IR transmission of fiber optic cable. Figure 35 shows a possible fiber cable assembly for this application.

The technology development difficulty which must be overcome in these applications is mitigating the effect of hydrogen exposure of the materials while producing the diamond film. The CVD processes based on carbon monoxide and oxygen, for example, could be used to avoid exposing the substrate to hydrogen. It is believed that extensive process development will be required before the hydrogen barrier applications can be of practical value.

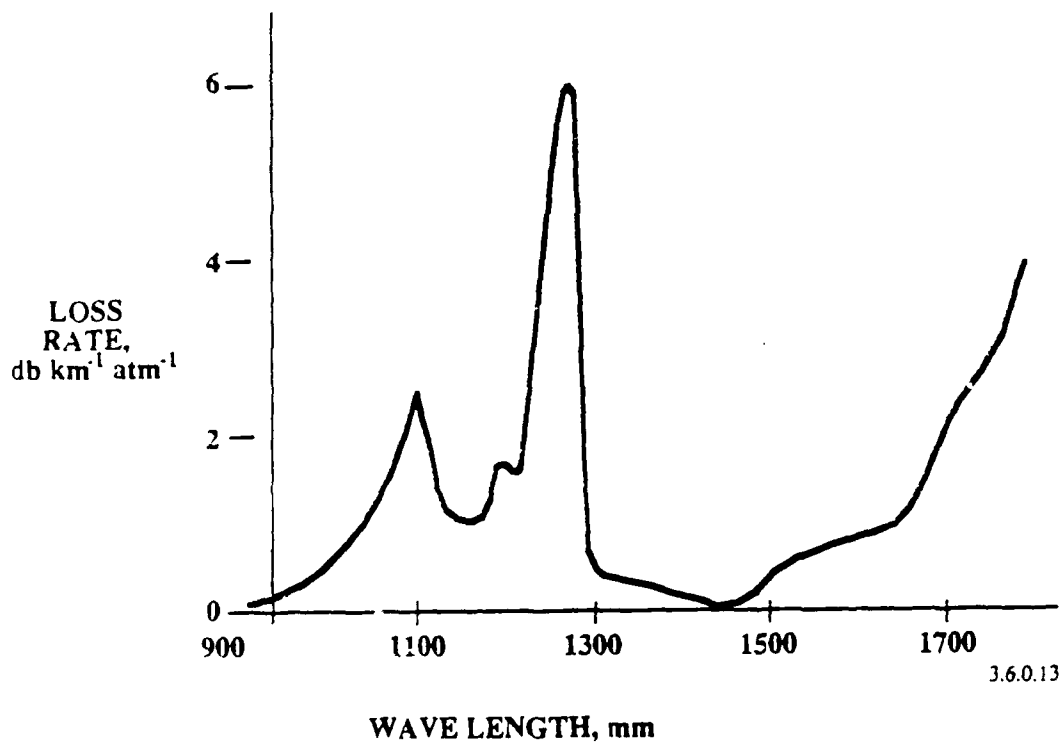


Figure 34. Effect of hydrogen absorption on signal transmission in fiber optic cable.

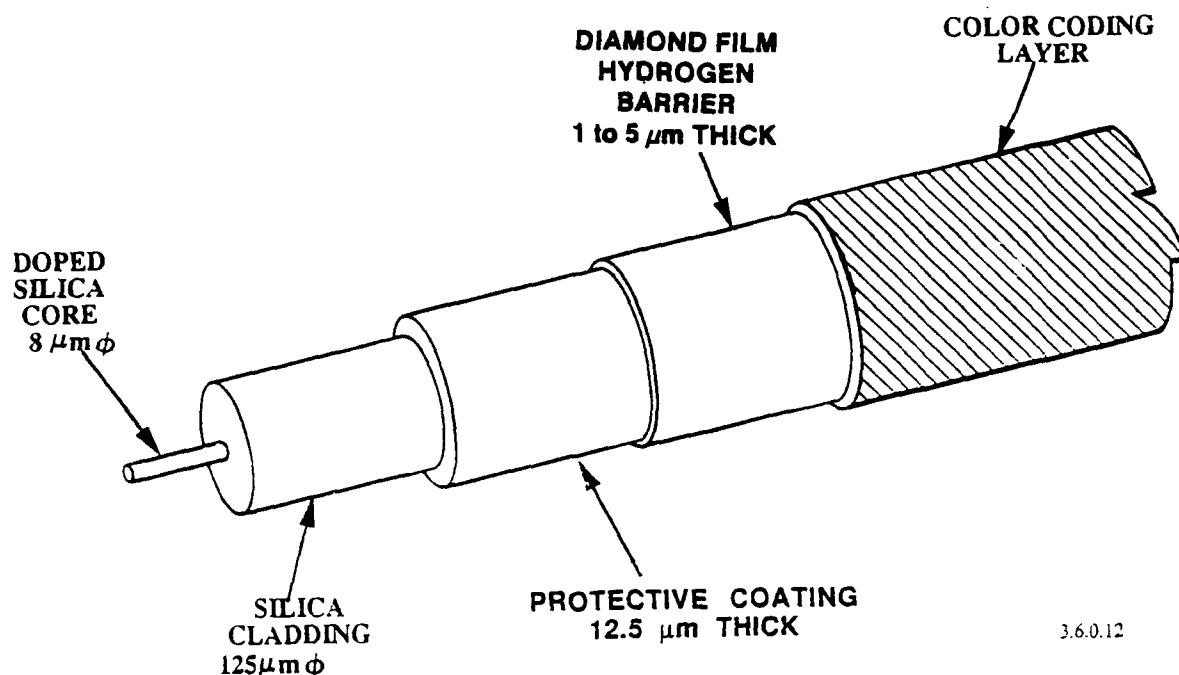


Figure 35. Application of diamond film to fiber optic transmission cables.

4.3.6 Chemical Attack Resistance--Diamond is impervious to chemical attack by reagents except molten carbide-forming metals up to moderately high temperatures (Ref. 20). Diamond does oxidize but, at 900 C, is much more resistant to oxidation than graphite. Measured oxidation rate of CVD diamond film is 0.0037 micron/min (8.7 microinch/hr) (Figure 19). Diamond is converted to graphite at elevated temperature. The conversion temperature is dependent on environment, being lowest in an oxidizing atmosphere (onset of graphitization occurs at about 1000 C, Ref. 21), but even in vacuum is complete by 1800 C.

Because the application temperatures are normally below 600 C, diamond film is a potential candidate for protection against corrosive propellants such as nitrogen tetroxide, chlorine pentafluoride, and fluorine.

Use of methane for booster engines is complicated by the fact that it is not a good coolant for high heat flux chamber applications. The design of choice for these applications is regeneratively cooled copper. However, trace amounts of sulfur in the methane attack the copper at elevated temperature, causing loss of cooling capability and failure (Ref. 22). Use of diamond film can protect the copper while enhancing the thermal transfer capability. Although diamond will not adhere directly to copper, its bonding can be accomplished by use of an intermediate layer of a few hundred Å of molybdenum or titanium.

Because of its oxidation resistance, high thermal conductivity, and low coefficient of friction, diamond may have advantages for protecting rubbing surfaces in oxygen environments such as oxygen turbopump rotating parts, bearings, seals, valve seats, and pintles.

5.0 PRELIMINARY PROPERTIES CHARACTERIZATION

Measurements were made of selected properties of synthetic diamond films as part of this program. Few properties have been well-characterized for CVD diamond, so, in most cases, the application analyses used properties measured for natural diamond.

Since the suitability of diamond film for a specific application is critically dependent upon its properties, selected characteristics were measured to reduce the uncertainty of the applications.

Of the many useful properties that could be measured, five were chosen for preliminary characterization. The measurements made were: (1) hydrogen diffusion rate, (2) hardness, (3) thermal cycling adhesion, (4) rupture strength, and (5) propellant corrosion resistance.

In all cases, the measurements made were for a small set of specimens and did not permit study of the effects of process parameters or process optimization. The results of the testing are summarized in Table 33; the testing is described in the following sections.

TABLE 33. Summary of Results of Phase III Preliminary Properties Characterization

Test	Procedure	Specimen Description	Number of Specimens Tested	Results
1. Hydrogen Diffusion (Crystallume)	1 atm ΔP across film, measured diffusion with mass spectrometer	0.5 micron thickness by DC plasma discharge on silicon	4	Transmission Range: 0 to 10^{11} torr-cm ³ sec ⁻¹
2. Microhardness (Crystallume/Stanford & Atlas Testing Laboratories)	Leitz Durimet with Vickers diamond indenter	10 micron on silicon	4	Hardness Range: 3820-3950 Kg mm ⁻²
		15 micron on molybdenum	1	Hardness Range: 10,000 Kg mm ⁻²
3. Thermal Cycle Adhesion (Crystallume)	Cycle specimen from ambient to 77 K 100 times	Titanium (Ti6Al4V)	Deposit not satisfactory	
		10 micron film on 0.76 mm molybdenum	4	Withstands test: no delamination or cracking
		Titanium (Ti5Al4V)	Deposit not satisfactory	
4. Rupture Strength (Crystallume)	Burst test of circular film	11 to 17 micron film on silicon	4	About 500,000 psi
5. Propellant Corrosion Resistance (AL)	Burst test of circular film	Free-standing film	4	No reaction

5.1 HYDROGEN DIFFUSION MEASUREMENTS

Hydrogen attacks some engineering alloys when stressed, such as titanium, resulting in loss of strength and early failure. Because of its tight crystal lattice, diamond should be a barrier to hydrogen diffusion. Therefore, one high-value application of diamond film is as a protective coating for highly stressed materials subject to hydrogen embrittlement. An example of such an application is for the impeller and other wetted components of hydrogen turbopumps.

To measure diffusion rate, thin (0.5 micron) diamond films were exposed to 1 atm differential pressure of hydrogen, and the leakage through the film was measured with a mass spectrograph.

Tests were performed to determine whether hydrogen diffusion through thin diamond films could be detected at ambient temperatures. Diamond was deposited on silicon and dies were fabricated by scribe-and-cleave methods. Subsequently, each diamond/silicon die was subjected to an anisotropic etch procedure to form a silicon grid array which served as pressure support for the diamond film. Each die was then mounted in an aluminum holder to permit further handling and testing. Four windows were fabricated using material from a single deposition run.

Each mounted die was then tested for helium leak integrity using a specially fixtured helium mass spectrometer (Veeco). This procedure also served as a pressure test of the mounted film, as one side of the film was maintained at 1.25 atm in He, while the other side was at 1×10^{-7} torr, the helium leak detector minimum base pressure.

Dies were then placed on a fixture attached to a mass spectrometer (Ametek Thermox-Dycor) which was used to detect hydrogen leakage. Each film was exposed to 1 atm of flowing hydrogen, with the other side directly connected to the mass spectrometer inlet. Hydrogen partial pressure was periodically recorded for at least 24 hours for each film.

A control part, using a thick silver-plated disc mounted in place of a diamond film, was tested to determine hydrogen transparency of the fixture and mounting adhesive. Hydrogen background was recorded over a period of several days to determine inherent instrument variability. Hydrogen partial pressure was also measured with hydrogen at fixed pressures flowing through a calibrated orifice attached to the mass spectrometer inlet to establish that the mass spectrometer operated properly.

All tests were performed at room ambient temperature, which ranged from 50 to 70 F. No hydrogen diffusion or leakage was observed in the four films tested, nor in the control part, to the limits of detection.

Diamond Film Deposition and Characterization--Diamond films were synthesized using a DC plasma-enhanced chemical vapor deposition reactor developed for diamond deposition. Deposition protocol was a proprietary method developed by Crystallume for production of X-ray spectroscopy windows. The technique consists of a two-stage deposition which results in a very densely nucleated first-stage diamond layer, followed by subsequent deposition of diamond under different deposition conditions. This protocol has been found to provide the structural integrity and mechanical properties necessary to provide leak-tight, pressure-tolerant windows.

Diamond film thickness was assessed by examination of a cleaved edge of the parent wafer following diamond deposition. Thickness varied between 0.5 and 0.55μ in the region from which dies were later fabricated. SEM examination of surface features showed a faceted film of normal appearance for the selected deposition conditions. Raman spectra were taken with an ISA U-1000 micro-Raman system, and were nominal for these deposition conditions, showing a diamond bonding peak at 1333 cm^{-1} and some

graphitic signal in the range of 1550-1650 cm^{-1} . Raman spectra taken near the wafer center and edge were essentially identical in signature and intensity, indicating good uniformity and thickness. Representative Raman spectrum from the parent wafer is shown in Figures 36 and 37.

After SEM thickness measurements and Raman spectroscopy, the diamond/silicon wafer was patterned for grid micromachining using lithographic techniques by an outside vendor. Anisotropic etch techniques were used to create trenches in the silicon which extended through the wafer to the diamond film. Etching action terminated when the etch front reached the diamond/silicon interface, as diamond is impervious to the etchant used for silicon removal. The resulting structure consisted of a thin, continuous diamond film attached to and supported by a set of silicon rails which comprised a support grid.

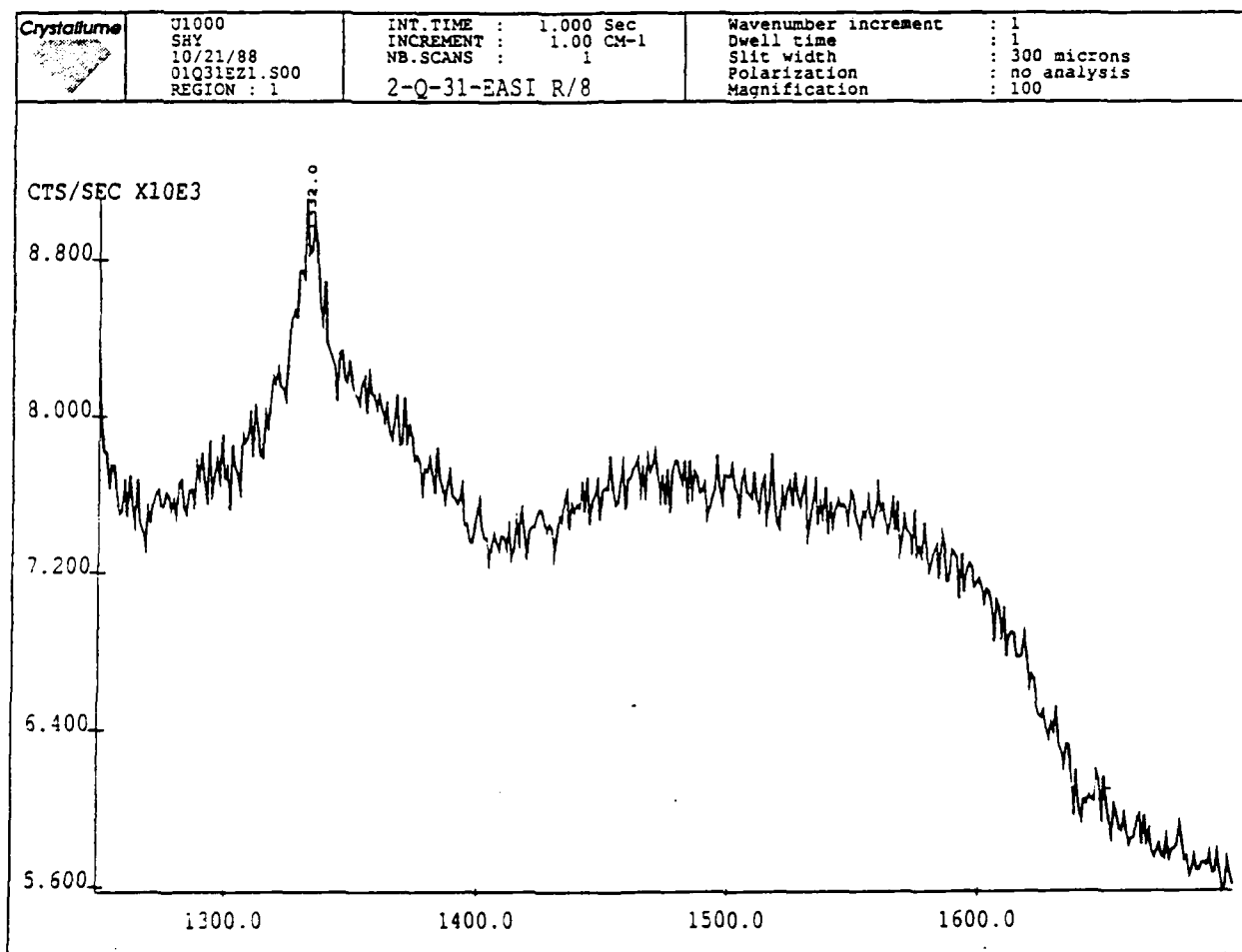


Figure 36. Raman spectrum, test specimen parent wafer at R/8.

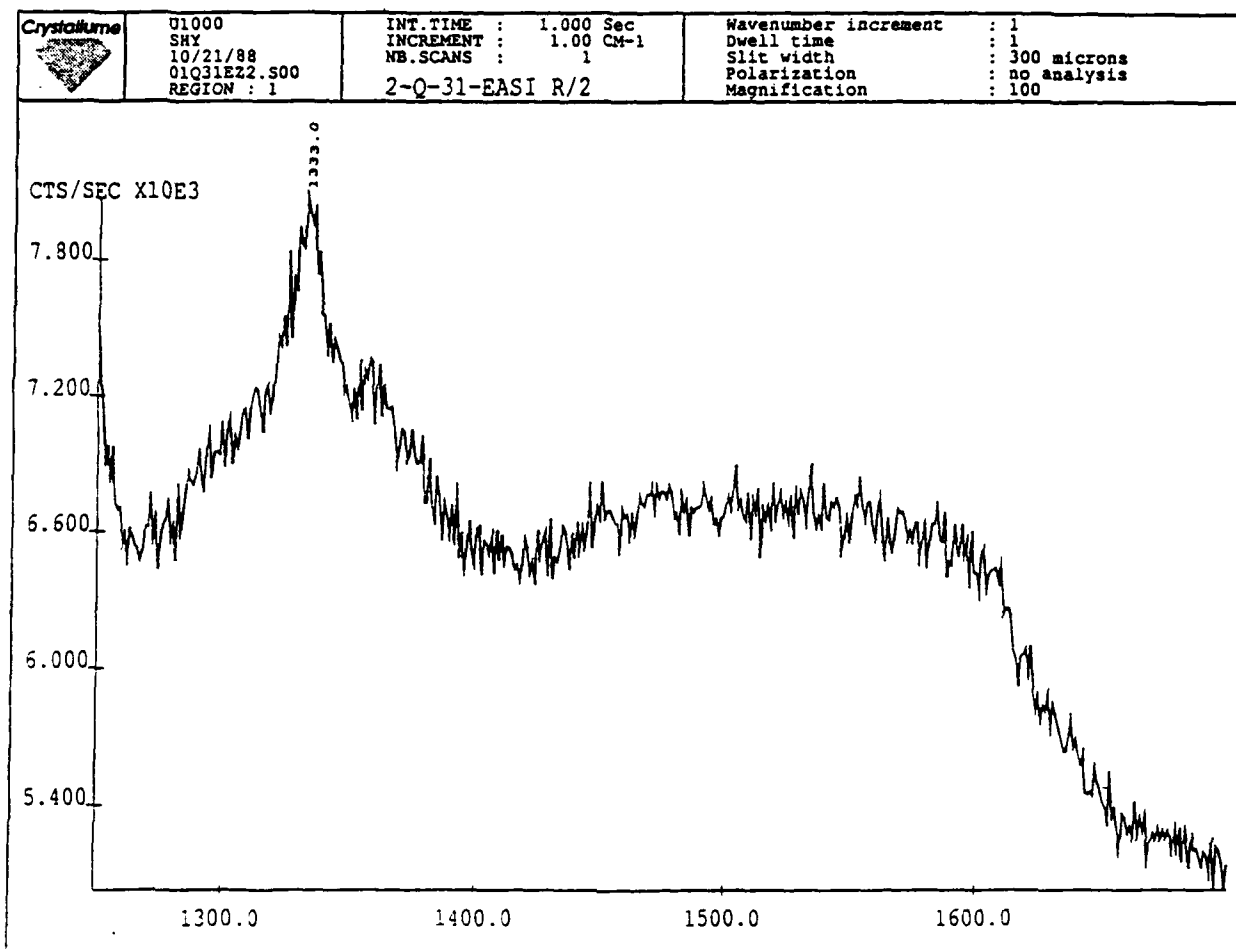


Figure 37. Raman spectrum, test specimen parent wafer at R/2.

Following patterning and etching, dice were separated from the parent wafer by scribe-and-cleave methods. Individual dies were inspected and mounted on an aluminum ring using low vapor pressure epoxy adhesive (TorrSeal, Varian). After 48 hours of cure time, mounted films were visually inspected for flaws prior to pressure testing.

The details of the wafer geometry are shown in Figure 38. The mounted wafer window assembly is shown in Figure 39. A section through the diamond film showing the silicon support structure geometry is given in Figure 40.

Pressure/He Leak Tests and Subsequent Fabrication--Diamond films mounted to aluminum rings were then tested for pressure and leak integrity using a helium leak detector (Veeco MS-20). This leak detector is a quadrupole mass spectrometer which is tuned for Atomic Mass No. 4 (helium). It provides an assessment of leak rate with a minimum sensitivity of 6×10^{-10} standard cubic centimeters/second. After the films were mounted to fixtures which communicate directly with the leak detector inlet, helium at

1.25 atm was introduced to the high-pressure side of the fixtures. Each film was monitored to determine whether helium leakage occurred. Prior experience in fabrication of thin diamond windows indicates that leakage, when present, is not a subtle matter but, rather, shows as an easily identified quantifiable leak rate. No leak was observed for any of the four windows, indicating that no film passed more than 6×10^{-10} sccs of helium.

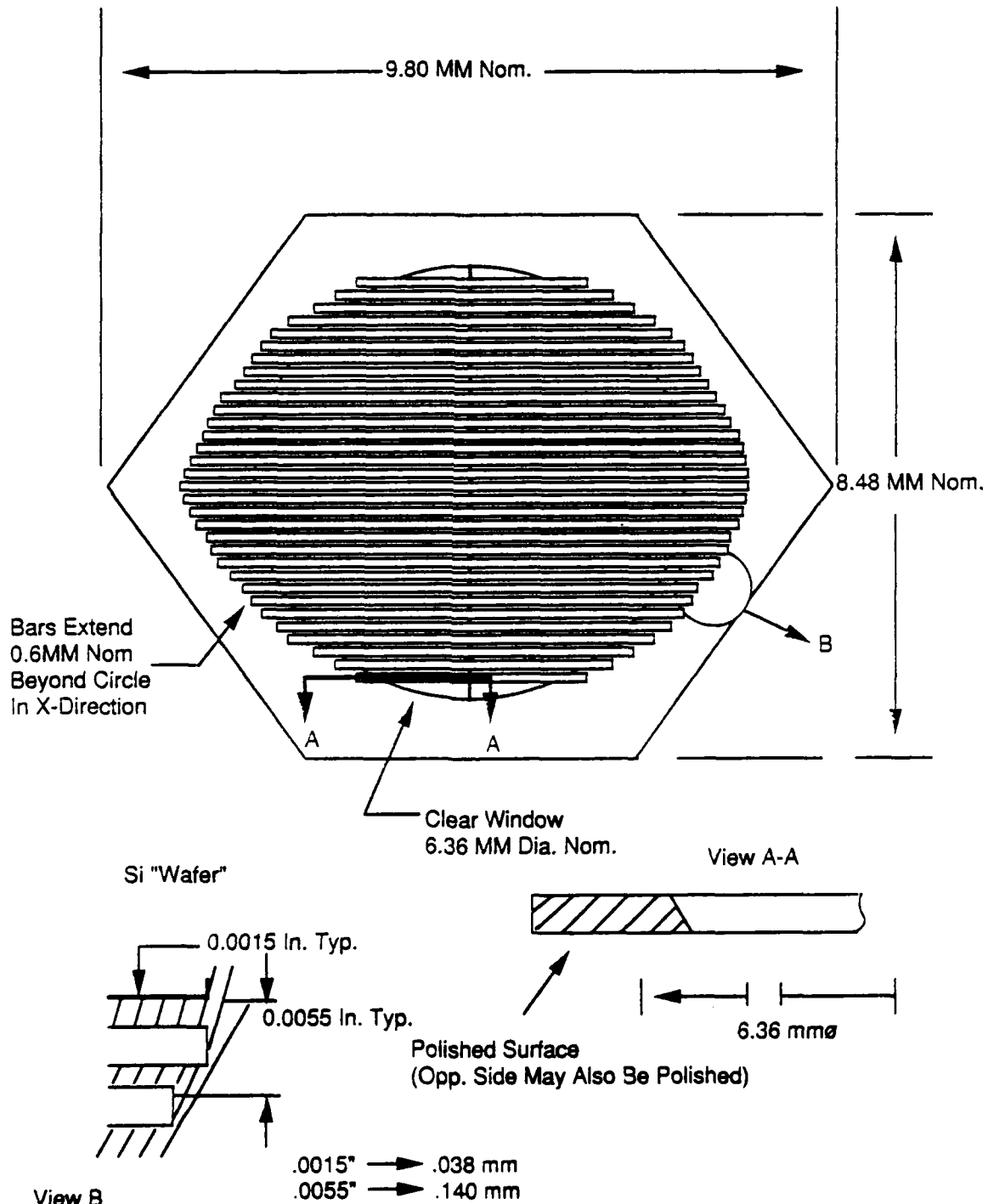
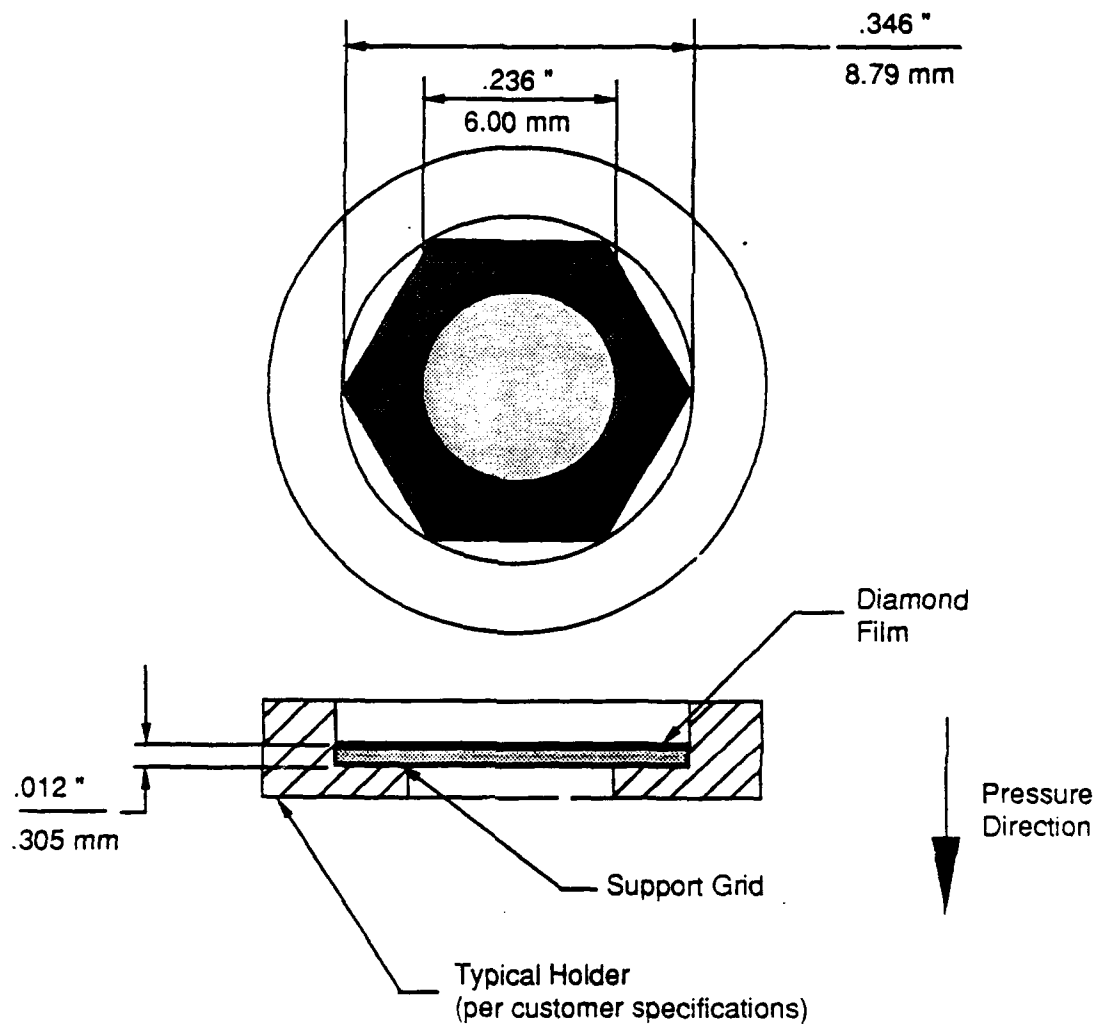


Figure 38. Silicon support for diamond X-ray window.



Specifications:

- | | |
|-----------------------------------|-----------------------------------|
| (1) Aperture Dia: | 6 mm |
| (2) Support Grid Dia: | 8.8 mm O.D. |
| (3) Transmission of Support Grid: | 70 % |
| (4) Thickness of Support Grid: | 0.3 mm |
| (5) Pressure Rating: | 1.25 atm(1.0 atm operation) |
| (6) Pressure Cycling: | 5000 + cycles; 1 atm |
| (7) Leak Rate (He): | $< 1 \times 10^{-9}$ atm cc / sec |

Figure 39. Diamond x-ray window.

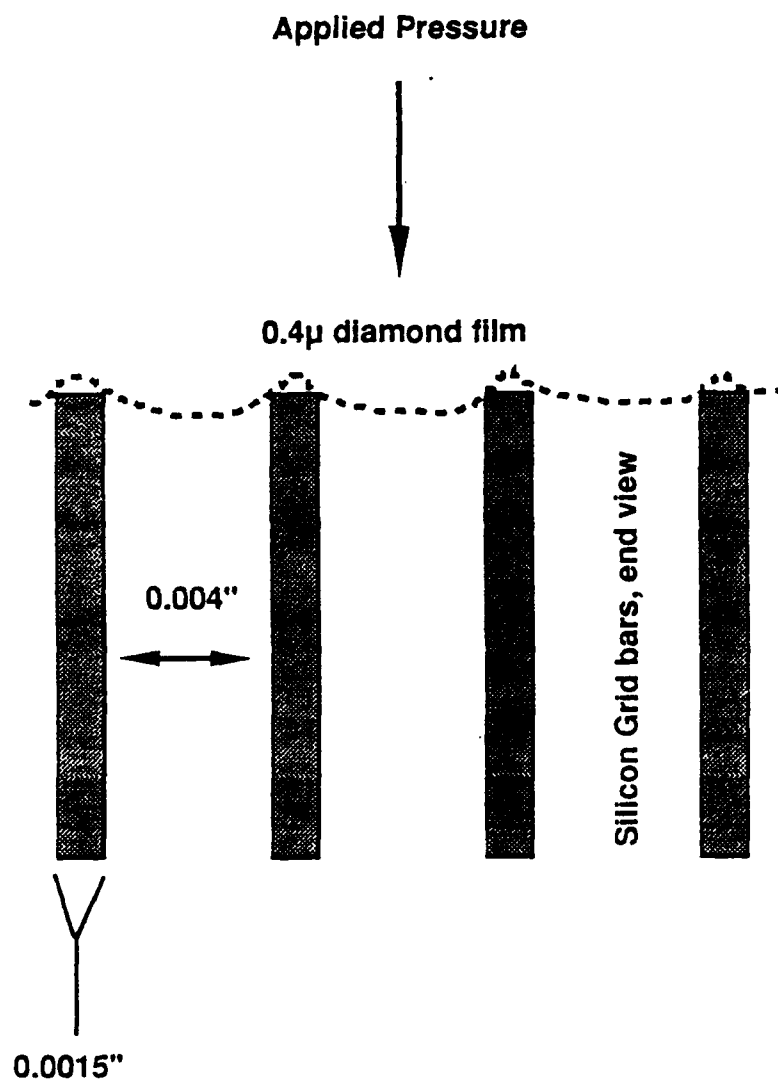


Figure 40. X-ray window schematic, diamond film on silicon grid, end view.

Each film on its aluminum ring was then, in turn, mounted using UltraTorr epoxy on a blind female VCR fitting (end cap) which had been drilled through with a 1/16" drill to provide a gas exhaust path. This provided the necessary mechanical interface for attachment to the mass spectrometer used for hydrogen detection. A blank VCR gasket (silver-plated nickel) was mounted to a fifth VCR end cap to provide a control test article for hydrogen transparency of the epoxy in the event hydrogen was detected while testing diamond films. Figure 41 shows a mounted specimen connected to the mass spectrograph. Figure 42 shows the overall setup.

Hydrogen Tests--Much the same procedure as was used for helium leak testing was used to measure hydrogen leakage/diffusion. The instrument used was a general-purpose mass spectrometer sensitive to species of atomic mass numbers between 1 and 100, inclusive. Data were displayed as partial pressure at specific mass numbers. The instrument has a small turbopump for generation of clean high vacuum, and routinely achieves base pressures (including test fixture) in the range of $7\text{--}9 \times 10^{-9}$ torr. When operated in normal mode (electron multiplier not engaged), the unit has a partial pressure quantization noise level of approximately $1\text{--}5 \times 10^{-11}$ torr, this being mainly a function of detector signal/noise performance. Enhanced sensitivity is available by engaging an electron multiplier option, but calibration across different mass numbers is thereby lost. Since hydrogen pressure must be arrived at by adding up at least three different species of hydrogen which can be produced in the quadrupole (H^+ , H_2^+ , H_3^+), the electron multiplier was not used.

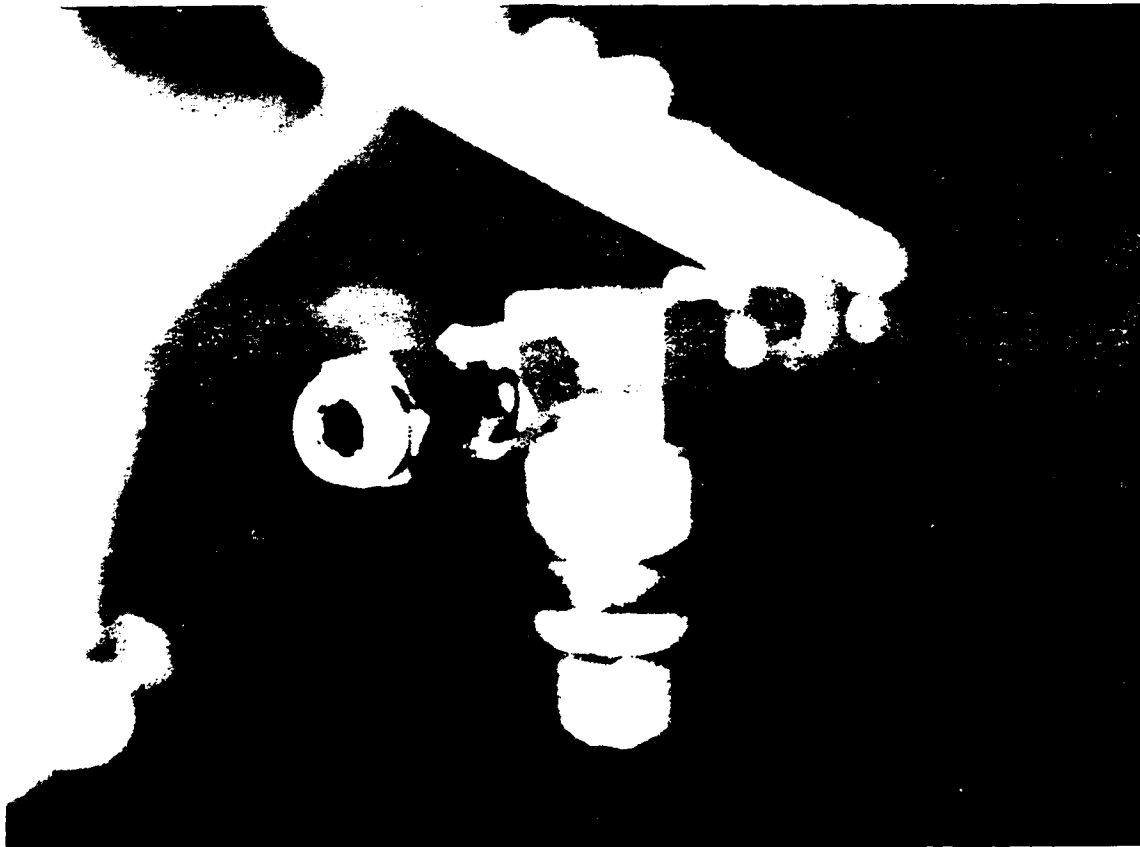


Figure 41. Detail of mounted window for diffusion measurements.

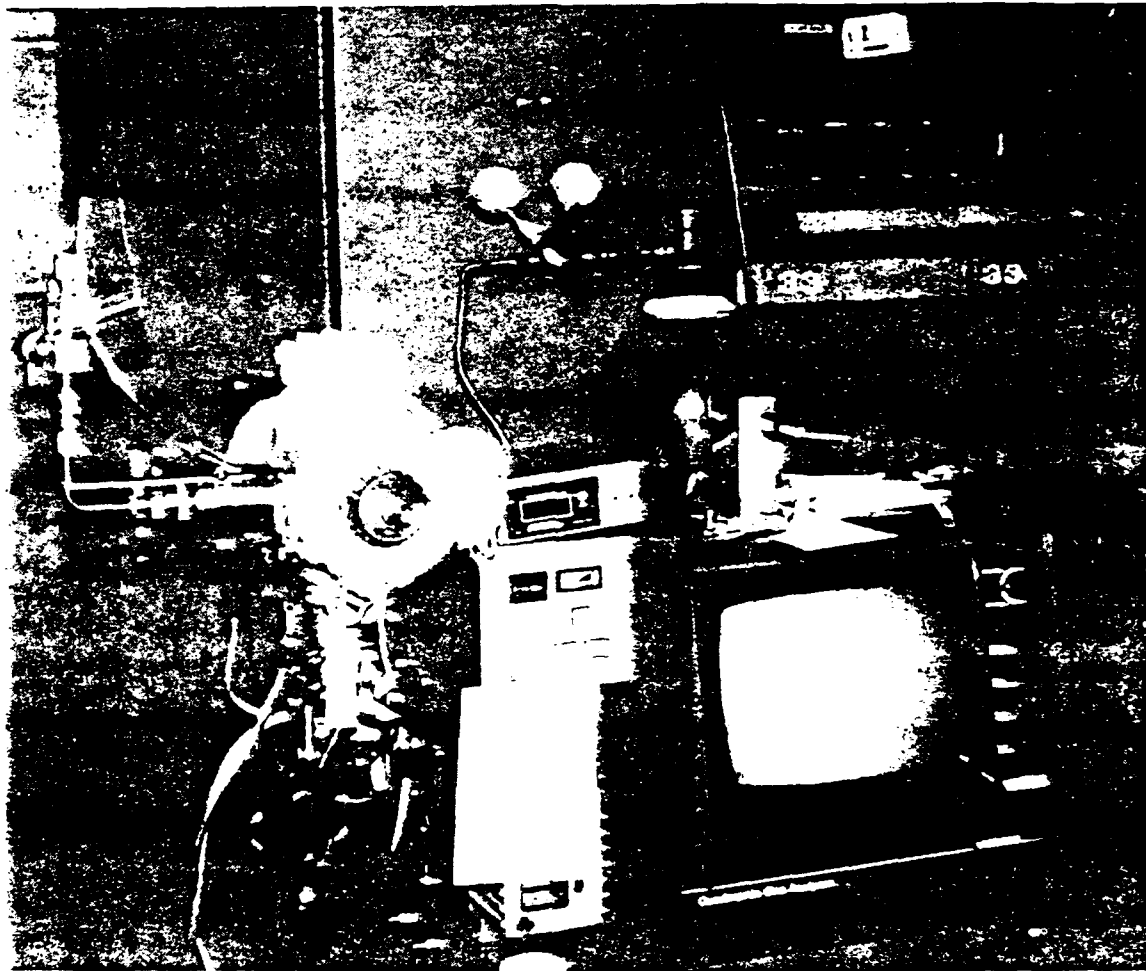


Figure 42. Mass spectrometer with mounted window under test.

Mass spectroscopy for species other than hydrogen and helium can present ambiguities due to overlap of different species at specific AMU values (e.g., AMU 28 can be CO and/or N_2), and due to double ionization effects (e.g., Ar^+ displays as AMU 40, but Ar^{++} displays as AMU 20). For these tests, however, no such complications arose, as all hydrogen species which could be created by the quadrupole analyzer lie within AMU 1-3, inclusive. The only other species which could potentially lie within this range which could be produced in sufficient quantity would be He^{++} , which would display as AMU=2. Presence of this species would have been disclosed by a stronger line at AMU=4, which was not seen.

Instrument stability was established by pumping the system with the sampling lines and valves open up to the film fixture head, on which was mounted the metal blank specimen. A heating blanket which enclosed the analysis head was set to operate at 103-110 C to provide continuous bakeout of adsorbed water from the head walls. The head was of electropolished stainless steel constructed in accordance with conventional high vacuum practices. The quadrupole was degassed by selecting the "degas" option, an operational mode which raises the temperature of the analyzer filaments for a few

seconds to boil off adsorbed gases from the quadrupole structure. After these measures were taken, the instrument was found to stabilize in the range of $7\text{--}9 \times 10^{-9}$ torr total pressure within 4 hours after being closed off from atmosphere. Further pumping for a period of 24 hours resulted in a hydrogen species background pressure of $\sim 1.5 \times 10^{-11}$ torr.

Minimum instrument sensitivity for a given species can be established from the values for detector noise floor and system pumping speed. For the Dycor mass spectrometer, the minimum detection sensitivity for hydrogen is approximately 1×10^{-11} torr (1.3×10^{-11} mbar), as stated above. The maximum pumping speed for hydrogen is given by the turbopump manufacturer (Balzers) as being 50 l/sec. Minimum detectable leak rate is therefore $[1.3 \times 10^{-11} \text{ mbar}] \times [50 \text{ l/sec}] = 6.5 \times 10^{-10} \text{ mbar l/sec}$, or $\sim 6.5 \times 10^{-10}$ sccs (Ref. 23). Performance of the Dycor mass spectrometer with hydrogen was essentially identical to that of the Veeco leak detector with helium. Mass spectrometer stability and equivalent base leak rate limits of detection are shown in Figure 43.

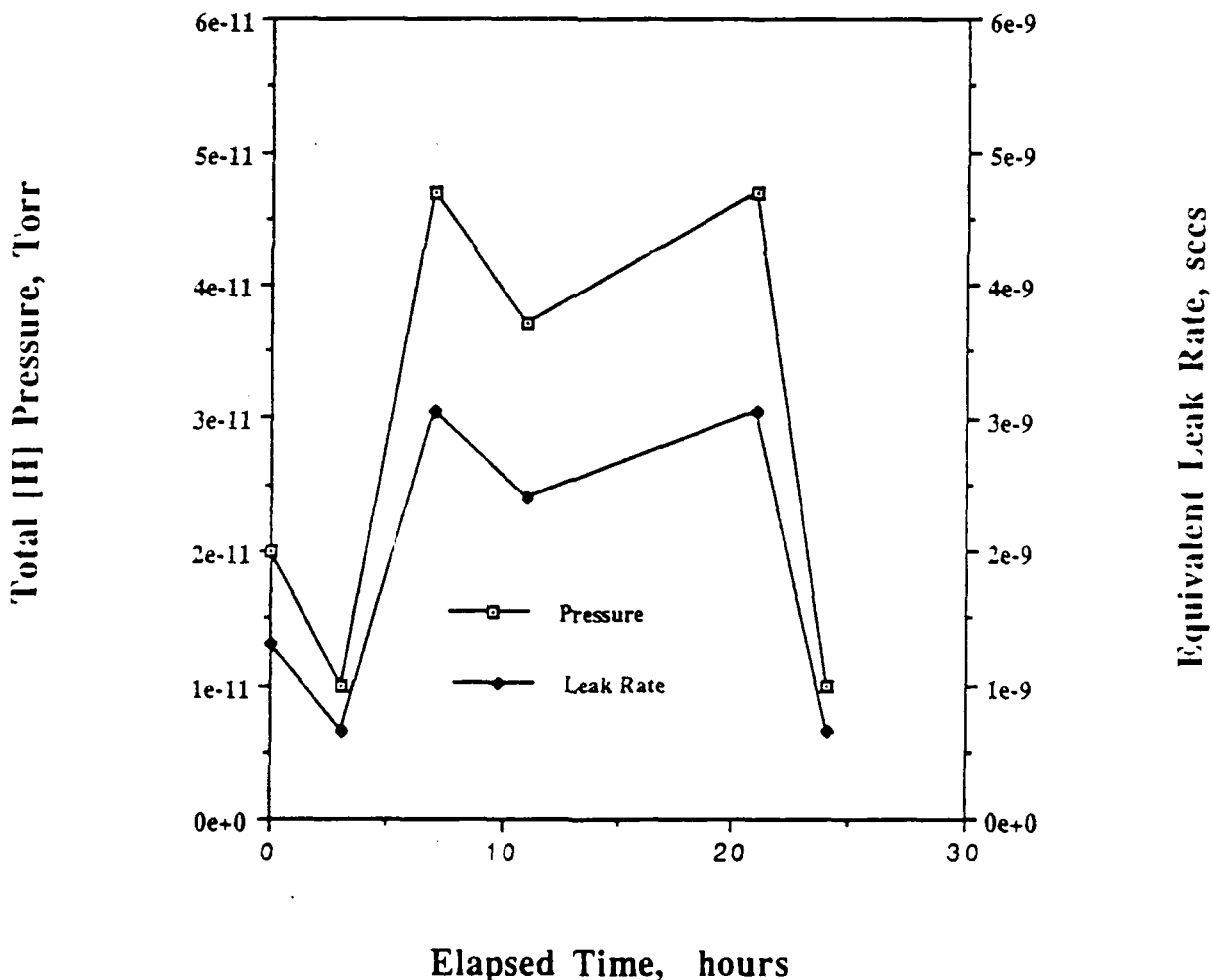


Figure 43. Mass spectrometer stability over 24 hours.

Hydrogen was applied to the test specimens by bagging the entire specimen in a plastic bag with a zip-lock-type of enclosure. The hydrogen inlet tube and mass spectrometer exhaust tube protruded from the bag by means of incomplete closure of the seal. Hydrogen was admitted through a mass flow controller (Vacuum General) at a flow rate of 150 sccm. Residual volume in the bagged specimen assembly was estimated at $<50 \text{ cm}^3$, ensuring replacement of residual air with hydrogen within a few minutes following onset of flow. This arrangement also prevented inadvertent overpressure of the specimen with hydrogen, which could have resulted in film rupture with catastrophic results for the mass spectrometer.

Each test specimen was mounted in the test fixture using a new VCR gasket. After mounting, the sample isolation valve was opened slowly to allow evacuation of the specimen fixture through the mass spectrometer. This step was performed with the filaments off to avoid filament oxidation and degradation of sensitivity. After the turbopump tachometer indicated resumption of normal operating speed, the filament power supply was turned on and the instrument was allowed to pump for at least two hours before background pressures were recorded. During this pumpdown, the small residual volume in the specimen fixture was heated with a hot air gun to between 100 and 150 C to bake out more rapidly residual water introduced during exposure to atmosphere. Following this bakeout, the filament was degassed.

Following establishment of a stable background pressure, the instrument was programmed to collect a reference background spectrum for storage. This background was subtracted from subsequent scans to provide maximum sensitivity and rejection of any signals from roughing pump oil which might have diffused upstream through the turbopump. Background subtraction is only available when the instrument is in "BAR" or "ANALOG" mode. Background subtraction does not operate in the "TABULAR" mode. Data were therefore recorded in the "BAR" mode. "ANALOG" mode provides slightly better resolution at higher mass numbers, but is not needed for $\text{AMU} < 15$.

After acceptable background storage and subtraction was established, a pretest spectrum ($T=0$) was recorded and printed. An example is shown in Figure 44. Hydrogen flow at 150 sccm was then initiated, and the initiation time was recorded. Data were taken at $T = +1 \text{ hr}$, $+8 \text{ hr}$, and $+24 \text{ hr}$ following hydrogen initiation. Figure 45 is a typical leakage spectrum taken after 24-hour exposure to hydrogen. The complete set of data printouts are given in Appendix D.

Test Results

Mass Spectrometer Stability: Samples taken at various intervals during a 24-hour period using a blanked-off VCR fitting in the test fixture showed variations in hydrogen partial pressure, defined as the sum of H^+ , H_2^+ , and H_3^+ partial pressures, from 0 (no H species detected) to $4.7 \times 10^{-11} \text{ torr}$, or an equivalent hydrogen flow rate of $\sim 6 \times 10^{-11} \text{ sccs}$. These measurements were obtained using background subtraction to remove the instrument's own background.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/7/89 9:14

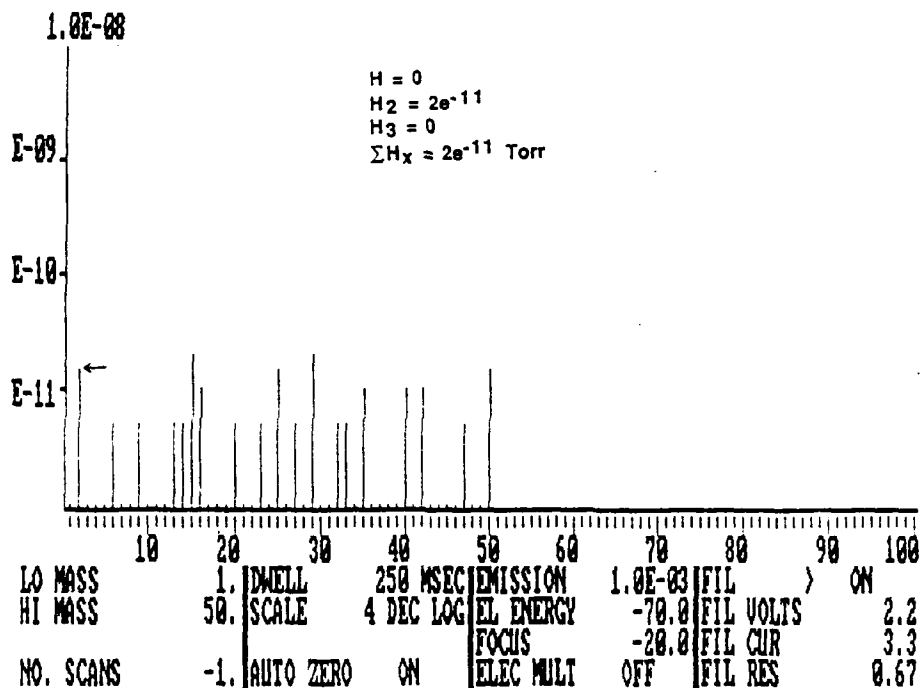


Figure 44. Stability test, $T = 0$.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/10/89 8:15

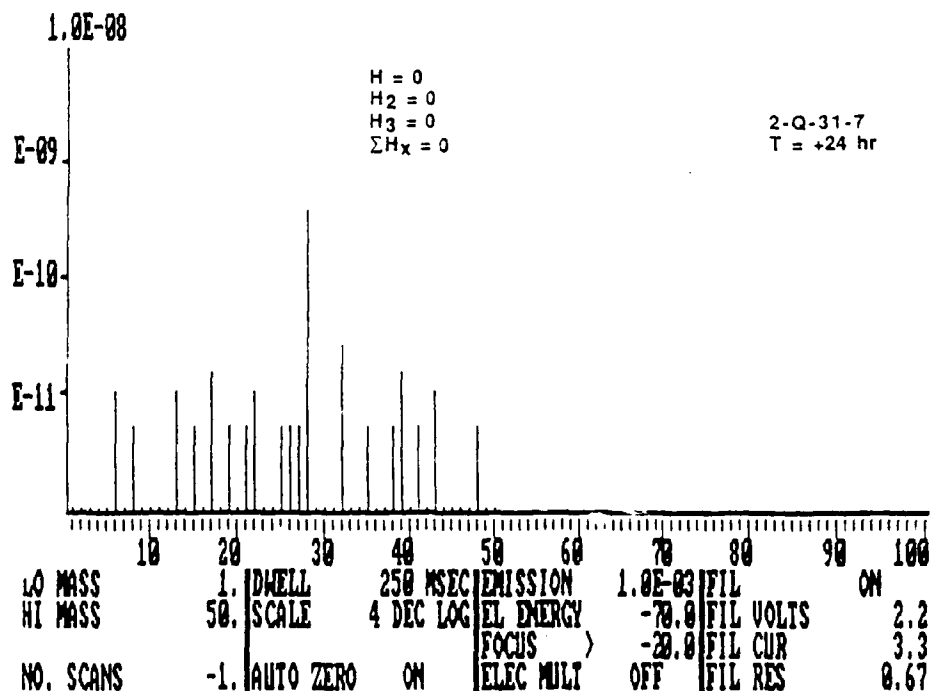


Figure 45. H_2 leakage spectra at 24 hours.

Diamond Films: The four samples tested and their hydrogen leakage pressure ranges are shown in Table 34 with the blanked-off control mount. The indicated leak rates vs. time are plotted in Figure 46.

Table 35 expresses the above data in ($\text{scc hr}^{-1} \text{ cm}^{-2} \text{ cm atm}$). Film area is derived using grid and aperture dimensions (shown in Figures 38 and 39) as follows:

- o Overall film/grid aperture = 6.36 mm diameter
- o Overall film/grid area = $3.18 \times 10^{-1} \text{ cm}^2$
- o Grid/film area ratio = 2.71×10^{-1}
- o film area = $8.6 \times 10^{-2} \text{ cm}^2$

TABLE 34. Measured Hydrogen Leakage Rate

Sample Number	Minimum H Pressure During The Run, torr	Derived Leak Rate Std $\text{cm}^3 \text{sec}^{-1}$	Maximum H Pressure During The Run, Torr	Derived Leak Rate Std $\text{cm}^3 \text{sec}^{-1}$
Blanked-Off Inlet	$0 \pm 1 \times 10^{-11}^*$	6.5×10^{-10}	4.7×10^{-11}	3.1×10^{-9}
2-Q-31-7	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}	8.7×10^{-11}	5.7×10^{-9}
2-Q-31-8	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}	8×10^{-11}	5.2×10^{-9}
2-Q-31-9	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}
2-Q-31-36	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}	$0 \pm 1 \times 10^{-11}$	6.5×10^{-10}

*Limits of detection.

TABLE 35. Calculated Hydrogen Diffusion Rate

Sample Number	Minimum [H] ($\text{scc hr}^{-1} \text{ cm}^{-2} \text{ cm atm}$)	Maximum [H] ($\text{scc hr}^{-1} \text{ cm}^{-2} \text{ cm atm}$)
Blanked-Off Inlet	$2.3 \times 10^{-8}^*$	1.1×10^{-7}
2-Q-31-7	2.3×10^{-8}	2.0×10^{-7}
2-Q-31-8	2.3×10^{-8}	1.8×10^{-7}
2-Q-31-9	2.3×10^{-8}	2.3×10^{-8}
2-Q-31-36	2.3×10^{-8}	2.3×10^{-8}

*Limits of detection.

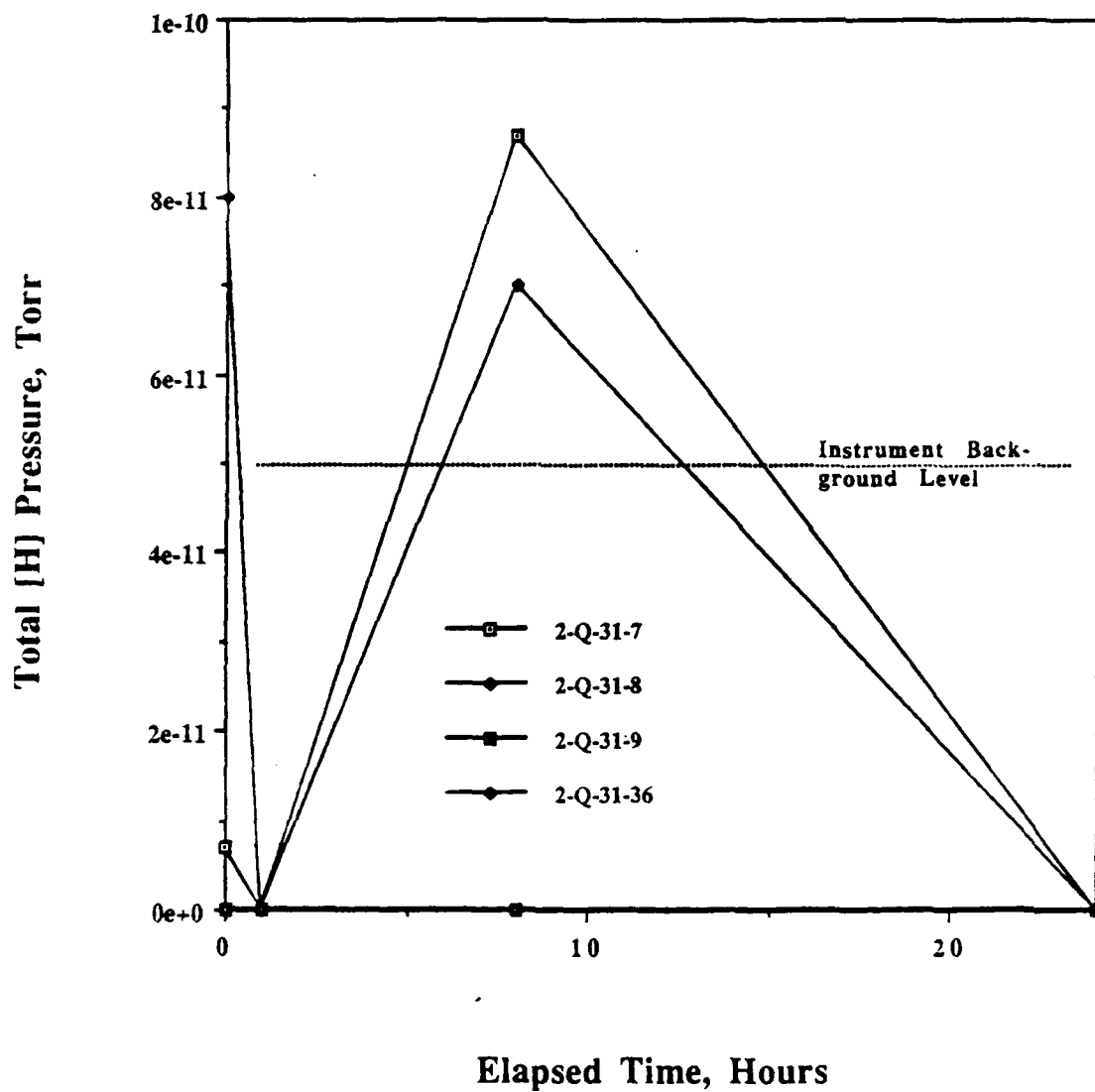


Figure 46. Hydrogen leakage through 0.5μ CVD diamond films on silicon support grids.

- o Film thickness = 0.5μ (nominal)
- o Hydrogen pressure = 1 atm

5.2 MICROHARDNESS MEASUREMENTS

Diamond coatings for bearings, optics, and cutting applications must have high hardness values to be competitive with present materials. Since natural diamond is the hardest material known, CVD diamond has potential for high hardness as well. Vickers hardness was measured using a diamond indicator. The Vickers hardness data were to have been used for fracture toughness measurements using the technique of Ref. 24. This requires measurement of the length of the microcracks surrounding the indentation. Since no cracks were observed, fracture toughness could not be determined.

Diamond films were deposited on two different substrates for hardness testing. Films approximately 10μ thick were deposited on $\langle 100 \rangle$ silicon strips approximately 3×0.75 cm, and films approximately 15μ thick were deposited on molybdenum sheet squares approximately 0.25×0.03 in. thick. Originally, hardness tests were to be run using Ti6Al4V substrates, but two deposition attempts on that alloy failed, yielding isolated diamond crystals rather than films.

First Test Series--Results were first obtained from four silicon substrates and one molybdenum substrate. Tests were performed at Stanford University, Department of Materials Science. The indentation tester was a Leitz Durimet, using a Vickers diamond indenter. No information was available on indenter orientation, but it is usual practice for indenter crystals to be oriented such that the hardest planes are presented to the specimen. For diamond, the hardest plane is the $\langle 111 \rangle$ plane and is usually given as $\sim 10,000 \text{ kg/mm}^2$. Calibration of the instrument prior to testing using a metallic Leitz calibration specimen gave an average calibration specimen hardness which was 0.992 of the stated hardness. Largest deviation during a series of five calibration indents was 0.988 of the stated standard hardness. Calibrations were performed using a 500-gram load. This load was somewhat heavier than usual, and was selected in anticipation of having to use high loads on diamond films. Indents were symmetric (A/B diagonal ratio ~ 1.00) and easily measured using calibration specimens.

Initial indenter load for diamond tests was 25 gm, and produced no detectable indentation. Indenter load was increased up to 3 kg. Indentations were seen only at 1 kg and 3 kg loads. The higher load cleaved some specimens, and results are reported only for the 1 kg load conditions. Indentations were small, difficult to measure, and generally poorly formed with irregular contours, in contrast with the indents formed during calibration. Indents were, in some cases, substantially asymmetric (A/B ~ 1.3). On later inspection with a Nomarsky optical microscope, evidence was found that the films had delaminated locally from the silicon substrate. This calls into question the values of the hardness data calculated below, suggesting that they underestimate film hardness due to fracture of the underlying silicon and subsequent deformation and fracture of the diamond film.

The single molybdenum substrate tested did not show an indentation which could be found after using a 1 kg load. A 3 kg load was not used on this specimen.

Another potential complication lies in the film morphology. The films tested showed a highly faceted morphology, a common feature of diamond films grown above 600 C. Raman and partial oxidation studies disclose that the films consist of polycrystalline diamonds with amorphous and/or graphitic material at the grain boundaries. The highly faceted polycrystalline nature of these materials suggests that microhardness may vary as a function of the average crystallite orientation ($\langle 111 \rangle$ is hardest) and that fracture toughness could vary in a complex manner, dependent on the grain boundary material and structure.

Second Test Series--Further tests of diamond films on molybdenum substrates were planned for execution at Stanford Materials Science Department facilities. Due to failure of the Durimet indenter, tests had to be carried out by a commercial laboratory. Diamond films on molybdenum were sent to Atlas Testing Laboratories at 6929 E. Slauson Avenue, Commerce, California 90040. Results were obtained for only one specimen (Die No. 10-N-96-9). Use of 1 kg loads on both Vickers and Knoop diamond indenters produced no visible indents, indicating that the film hardness is comparable to the indenter hardness. The surface appearance of this specimen is shown in Figure 47.

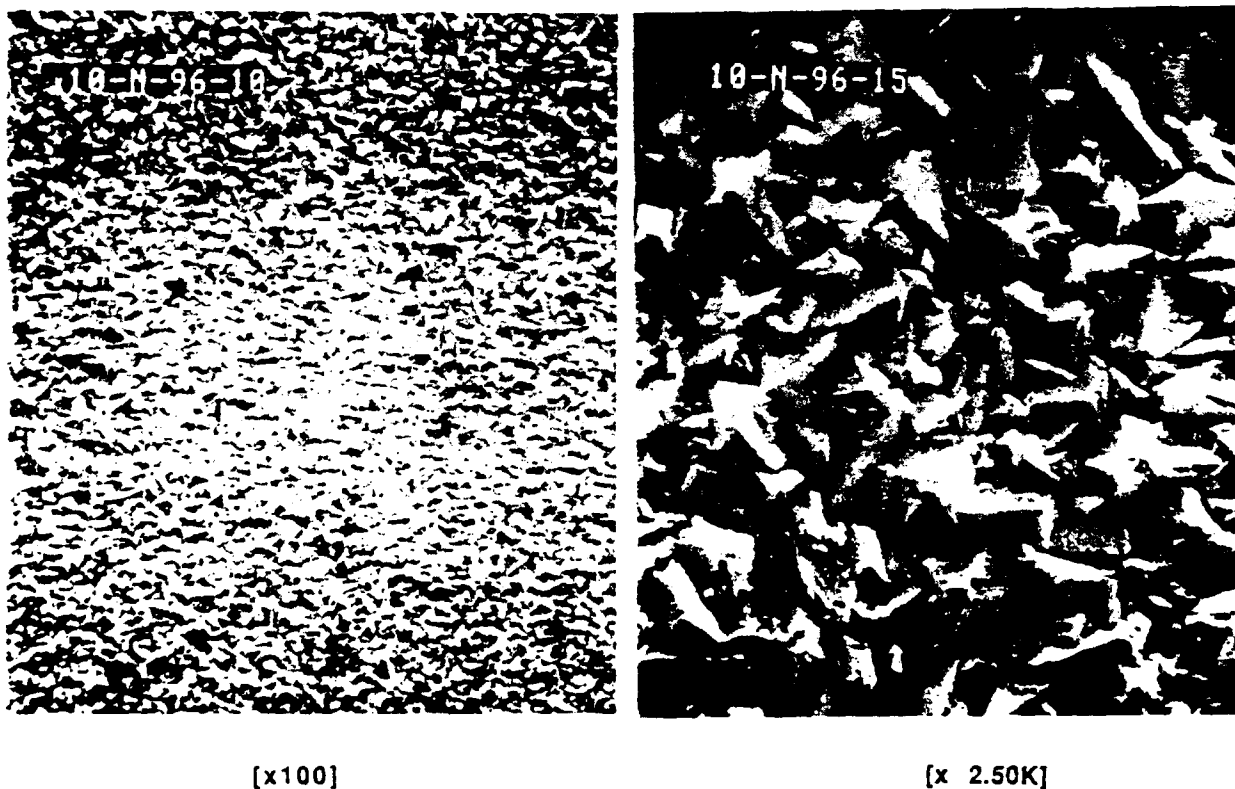


Figure 47. Surface appearance of hardness specimen.

Hardness measurements from the five silicon specimens and one molybdenum specimen are shown in Table 36.

Results of these tests suggest that CVD diamond films tested exhibit hardness at least comparable to the hardness of diamond indenters. Although scatter in calculated hardness values for films on silicon is relatively low, these data are probably inaccurate due to effects of substrate damage at high loads. A strong substrate dependence may be apparent, as no indentation was found on diamond films deposited on molybdenum sheets, even though loads were the same as those used for diamond on silicon. This may, in part, reflect a difference in adhesion between CVD diamond films and silicon or molybdenum substrates.

Fracture Toughness--Attempts were made to find and measure cracks propagating from the tips of indents formed during microhardness testing. Cracks were not found using the Durimet microscope, nor did later inspection using Nomarsky interference contrast illumination disclose cracks. If cracks were present, it is likely that they would have been obscured by the zone of delamination which apparently formed around the indents. Because of this, no fracture toughness calculation was possible.

Basic measurements from the hardness tests of the silicon substrates are given in Table 37. The hardness determination method is illustrated in Figure 48, along with a sketch of the possible delamination zone appearance. The hardness data for the diamond on silicon are plotted in Figure 49.

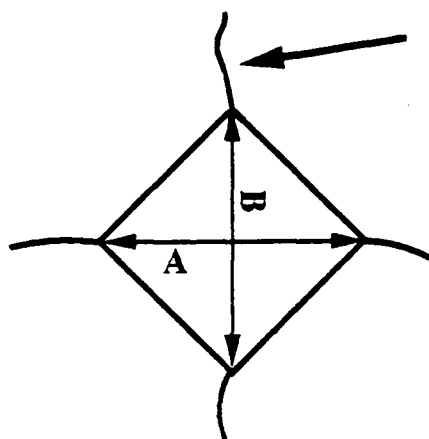
TABLE 36. Measured Diamond Film Hardness

Die Number*	Calculated Vickers Hardness, Kg mm ⁻² (1 Kg load, five indents)	Average Hardness, Kg mm ⁻²
3	8560, 8890, 9430, 8510, 8880	8850
4	9300, 8790, 9010, 9300, 8350	8950
5	Die cracked when loaded	-
6	9230, 8940, 8230, 8900, 9390	8940
7	8700, 8760, 9040, 8500, 9110	8820
10	No indentations found	Same as indenter (~10,000)

*Data for Dice Nos. 3, 4, 5, 6, and 7 are from Run No. 10-N-84-MWSI, diamond on silicon substrate. Die No. 10 is from Run No. 10-N-96-MWMO, diamond on molybdenum substrate.

TABLE 37. Hardness Calculations

Hardness Calculations, Silicon Substrate					
Die #	Diagonal A, μ	Diagonal B, μ	Average Diagonal, μ	Load, g	Hardness, kg/mm ²
10-N-84-3					
Indent #					
1	14.7	14.7	14.72	1000	8564
2	13.2	15.7	14.45	1000	8887
3	13.4	14.7	14.03	1000	9428
4	14.5	15.0	14.76	1000	8512
5	14.3	14.6	14.45	1000	8881
				avg.	8854
10-N-84-4					
Indent #					
1	14.7	13.6	14.12	1000	9301
2	14.1	15.0	14.53	1000	8790
3	14.5	14.2	14.35	1000	9005
4	13.6	14.7	14.13	1000	9295
5	14.6	15.2	14.90	1000	8353
				avg.	8949
10-N-84-6					
Indent #					
1	14.9	13.5	14.18	1000	9229
2	16.2	12.6	14.40	1000	8943
3	14.8	15.2	15.02	1000	8225
4	13.7	15.2	14.44	1000	8900
5	12.9	15.2	14.05	1000	9394
				avg.	8938
10-N-84-7					
Indent #					
1	12.5	16.8	14.60	1000	8700
2	15.7	13.4	14.55	1000	8759
3	14.0	14.7	14.33	1000	9037
4	13.8	15.7	14.77	1000	8500
5	12.5	16.1	14.27	1000	9113
				avg.	8822



Crack leads

Vickers
Microhardness
= $[(1854.4) L]/D^2$

L = Load in grams
D = average diagonal
length in μ

Ideal Indent Pattern

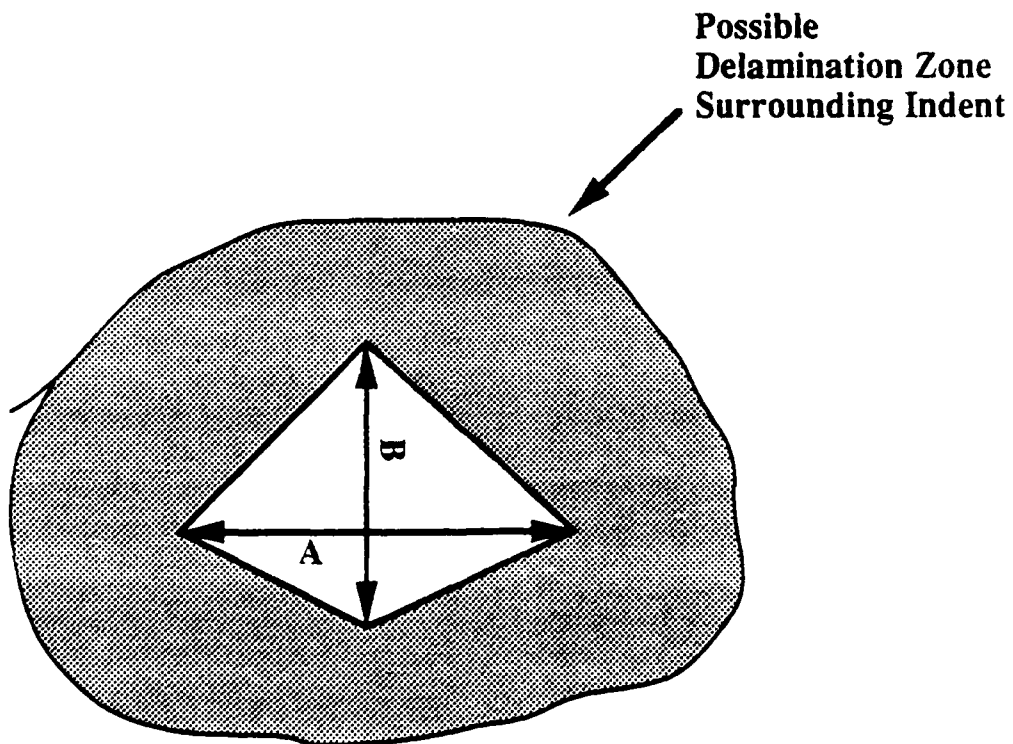


Figure 48. Asymmetric indent on CVD diamond on silicon samples.

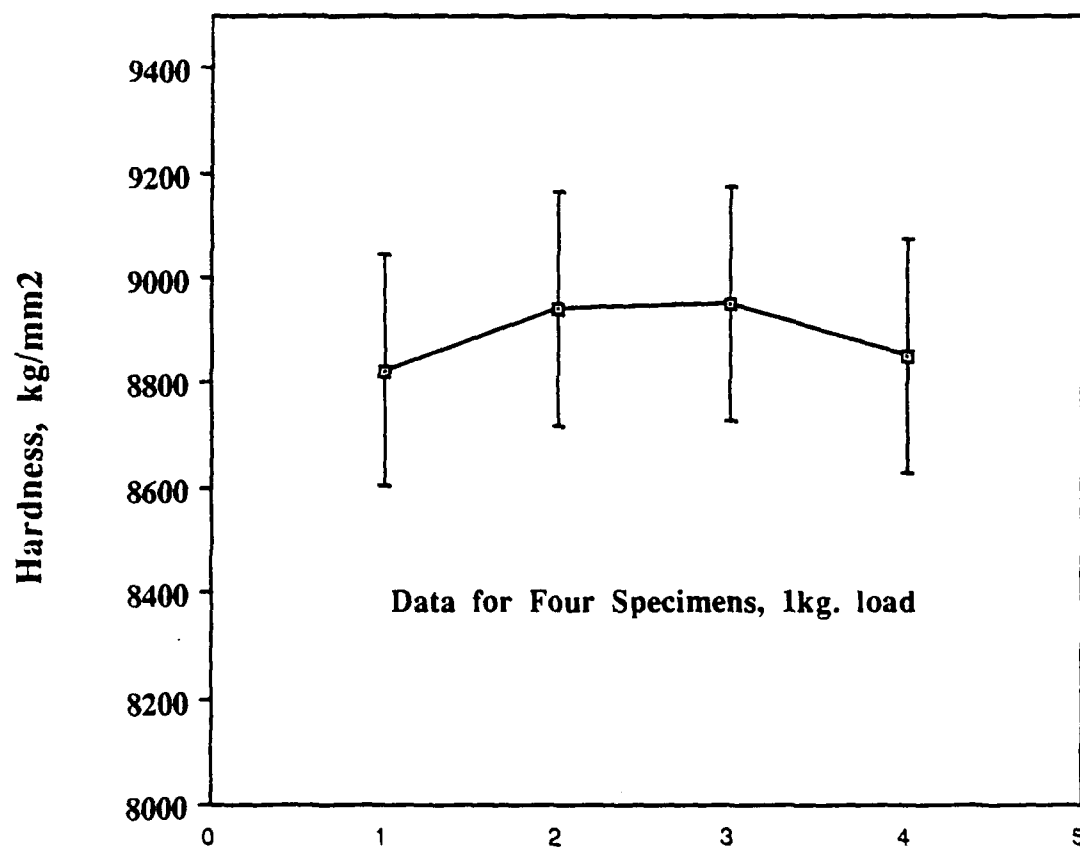


Figure 49. Vickers hardness. CVD diamond on silicon substrate.

5.3 THERMAL CYCLING ADHESION

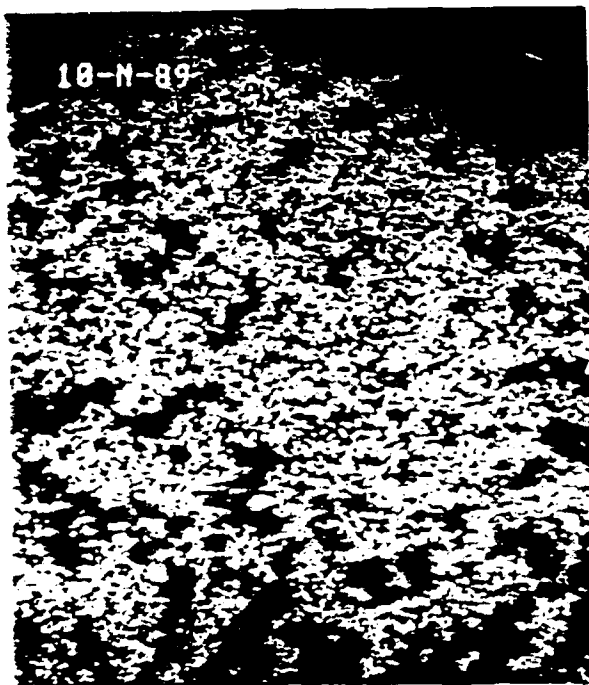
Many aerospace bearing and protective coating applications of diamond film require that the film-substrate bond withstand repeated thermal cycling to cryogenic temperatures. In any coating application, the bond to the substrate is a potential failure point. Repeated cycling of the bond from room temperature to liquid nitrogen temperature was chosen as a practical test of the adhesion capability of the diamond film.

Although the intent of thermal cycling tests in this program was originally to use specimens deposited on Ti6Al4V substrates, two deposition attempts on specimens of that material failed to produce coalesced films. Diamond was formed but, in large, isolated crystallites rather than dense films. An SEM photograph showing diamond crystallites on titanium from one of the two anomalous depositions is presented in Figure 50 (Deposition No. 10-N-89-MWTI). Prior deposition on titanium and titanium alloys has shown formation of adherent diamond films. Cause of these deposition failures is not known at this time. In the interest of obtaining thermal cycling data from diamond films on metallic substrates, molybdenum was chosen as an alternate material.

Deposition substrates were 1/4-in. squares cut from 0.03-in. molybdenum sheet procured from Thermoshield, Menlo Park, California. Metallurgical history of the substrates was not available, but the material's microstructure was consistent with its being a powder metallurgy product produced by repeated rolling compaction of molybdenum powder.

Substrates were prepared for deposition by abrasion with 1 μ diamond powder suspended in isopropanol. This procedure promotes nucleation of diamond, resulting in high nucleation density and reduced nucleation latency. Coalesced diamond films were formed which covered the entire upper surface of each specimen and which wrapped over the edges to varying degrees. A representative Raman spectrum of one of the films is shown in Figure 51. Inspection of the samples after deposition disclosed one specimen with obvious delamination and cracking over half of the substrate. This specimen was situated at the periphery of the deposition zone and was operated at a reduced temperature. Cause of the delamination on this specimen is not known at this time. This specimen was excluded from thermal cycling.

Specimens were handled carefully to avoid bending the substrate and cracking or delaminating attached films. Handling precautions included use of Teflon forceps (minimizes stress concentration at contact area) and immersion fixture to reduce the probability of films being chipped loose by impact with a hard-surfaced holder during the violent boiling action which accompanied immersion in LN₂. Because SEM examination required that the specimens be clamped with moderate force and therefore with some distortion, it was decided to perform microscopic examinations with a Nomarsky optical microscope. Prior experience at Crystallume in looking for localized adhesion failure suggested that optical inspection (particularly with Nomarsky phase-contrast methods) would be more likely to disclose delamination than SEM inspection.



(25X)



(510X)



(2.5K)

Figure 50. SRU photos of unsatisfactory deposition on Ti6Al 4V specimens.

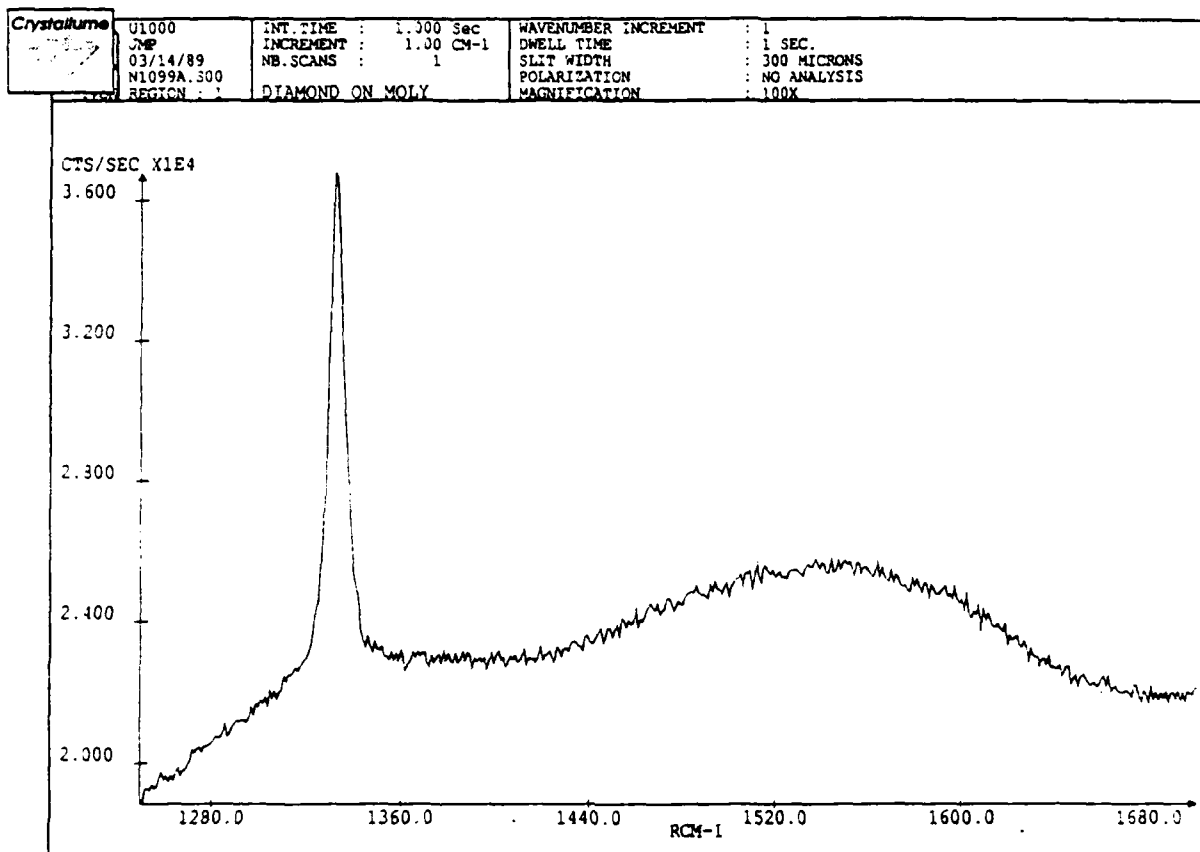


Figure 51. Thermal cycling die #11, center.

Examination of the delaminated specimen suggested that it would be difficult using a normal incidence view of the specimens to discover delamination between the diamond film and the molybdenum substrate. The diamond films were sufficiently thick to preclude seeing through to the substrates with either optical or electron microscopy methods (e^- beam penetration depth in diamond at 20 Kv accelerating voltage is approximately $1-3 \mu$, insufficient to see through these films). Thus, local delamination could potentially occur without detection by the inspection means available. Therefore, it was decided that evidence of delamination due to thermal cycling might be best detected at the edges of the film, where a clear interface between the diamond and molybdenum could be seen. Monitoring the appearance of this interface would probably provide the earliest and most sensitive indication of delamination. Photographs of interface contours were taken for each specimen using an identified edge to provide a record of interface change during testing. In addition, the surface of each specimen was visually inspected with a 10X lens after each thermal cycle to detect film cracking, if present.

Thermal cycling protocol consisted of placing the specimens in a Teflon die holder and plunging them into liquid nitrogen (77 K) in a 2-liter container using the apparatus shown in Figure 52. Specimens were oriented vertically and presented little cross-section to nitrogen bubbles caused by boiling on immersion of the fixture. Specimens were not mechanically constrained by the holder. Immersion time was at least one minute, which was found to be sufficient time for LN_2 boil-off to subside to pre-immersion rates. Specimens were then removed and allowed to stand until 5 minutes after all condensation



Figure 52. Thermal cycling components.

ice had melted. This time varied with local humidity, but was never less than 11 minutes. The immersion cycle was then repeated. Specimens were inspected at intervals of 5 immersions and photographed at intervals of 25 immersions, to 100 total immersions. Tests were performed over four days, with 25 immersions per day.

Results--No thermally induced delamination of diamond films from molybdenum was noted during the course of these tests. Sample photographs are presented in Figures 53 through 56. Although photographs were taken every 25 cycles, only the pretest and 100-cycle photos are shown because of the lack of change in visual appearance. Labels in the lower left corners are sample numbers, lower right corners are magnifications, and upper right corners are thermal cycling numbers, where 0 = precycling.

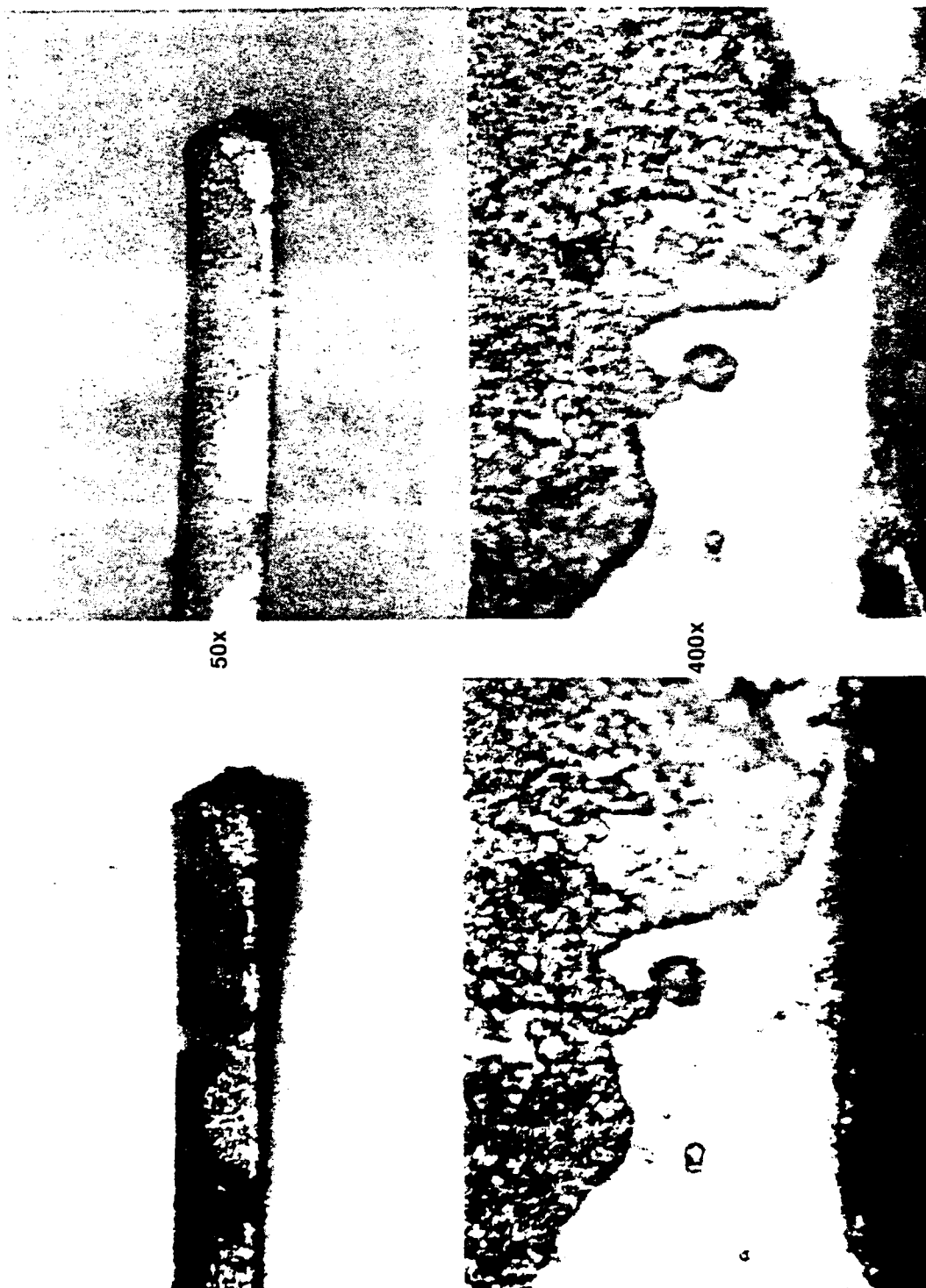
Examination of the specimens and of micrographs taken of each specimen showed that the reference film edges remained unchanged from their precycling contours. No removal of crystallites was noted, indicating that thermal cycling was insufficient to overcome adhesion between the molybdenum and deposited diamond even in those areas in which the film had not fully coalesced.

A final test of film adhesion was performed which consisted of mounting each specimen to double-sided tape (deposition side up) and performing a pull test with single-sided tape attached to the exposed diamond film. The single-sided tape has a weaker bond with the diamond film than did the tape in contact with the reverse of each specimen. This test was carried out after all thermal cycling was done because of its potential for complication of the results by production of deformation-induced film fracture and delamination. Tapes were examined after pulling to locate film fragments. None was found.

5.4 RUPTURE STRENGTH

Natural diamond has a measured tensile strength of 0.5×10^6 psi and a theoretical tensile strength of 16×10^6 psi. Burst tests of thin diamond films during previous production testing of X-ray windows gave loads at failure initially interpreted by plate theory as being in the range of 3×10^6 psi. Such a strength value would open up many structural applications for diamond film. Since the window tests were made with very thin (0.5 micron) films, the test procedure was modified to use thicker films which would be practical for structural application. Further detailed analysis of the early window data using membrane theory prior to testing the thick films indicated that the rupture data should be interpreted as representing tensile strengths in the 0.25×10^6 psi range.

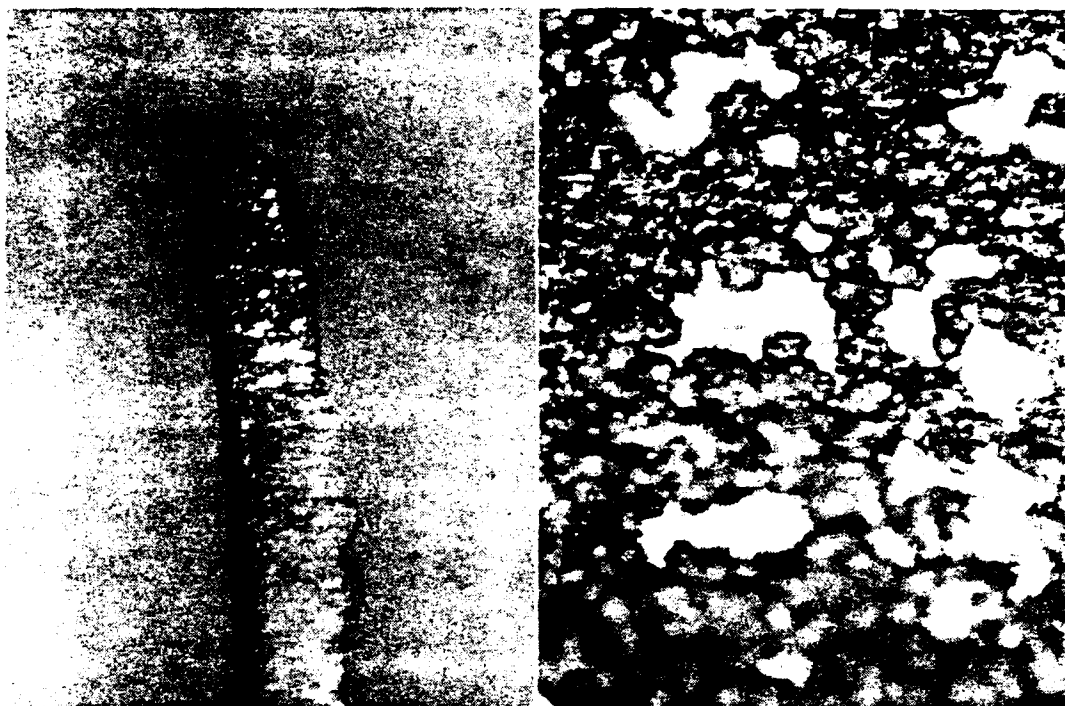
To obtain data on tensile strength for this program, a burst test procedure was designed for using the thicker films under conditions which would allow more straightforward interpretation of the data. Free-standing diamond films were subjected to increasing differential pressure until film rupture occurred in order to determine tensile strength at rupture. One object of these tests was to determine how tensile strength scaled with film thickness.



Pretest

After 100 Cycles

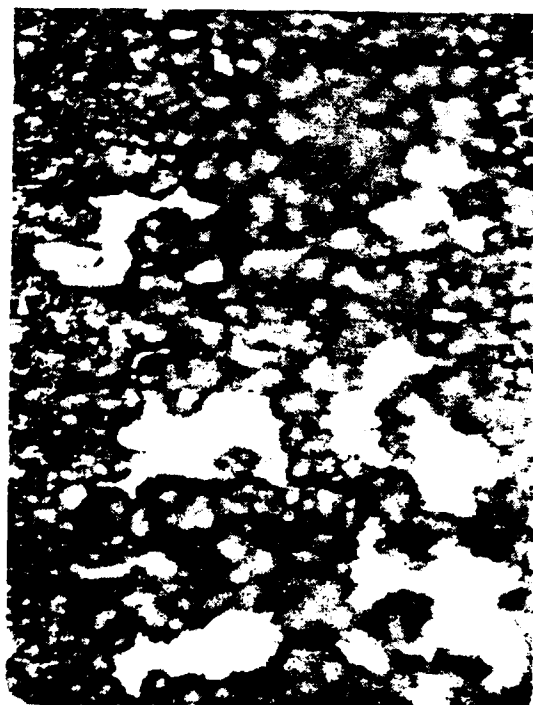
Figure 53. Appearance of diamond film interface at edge of
specimen 10 M 05 14



50X

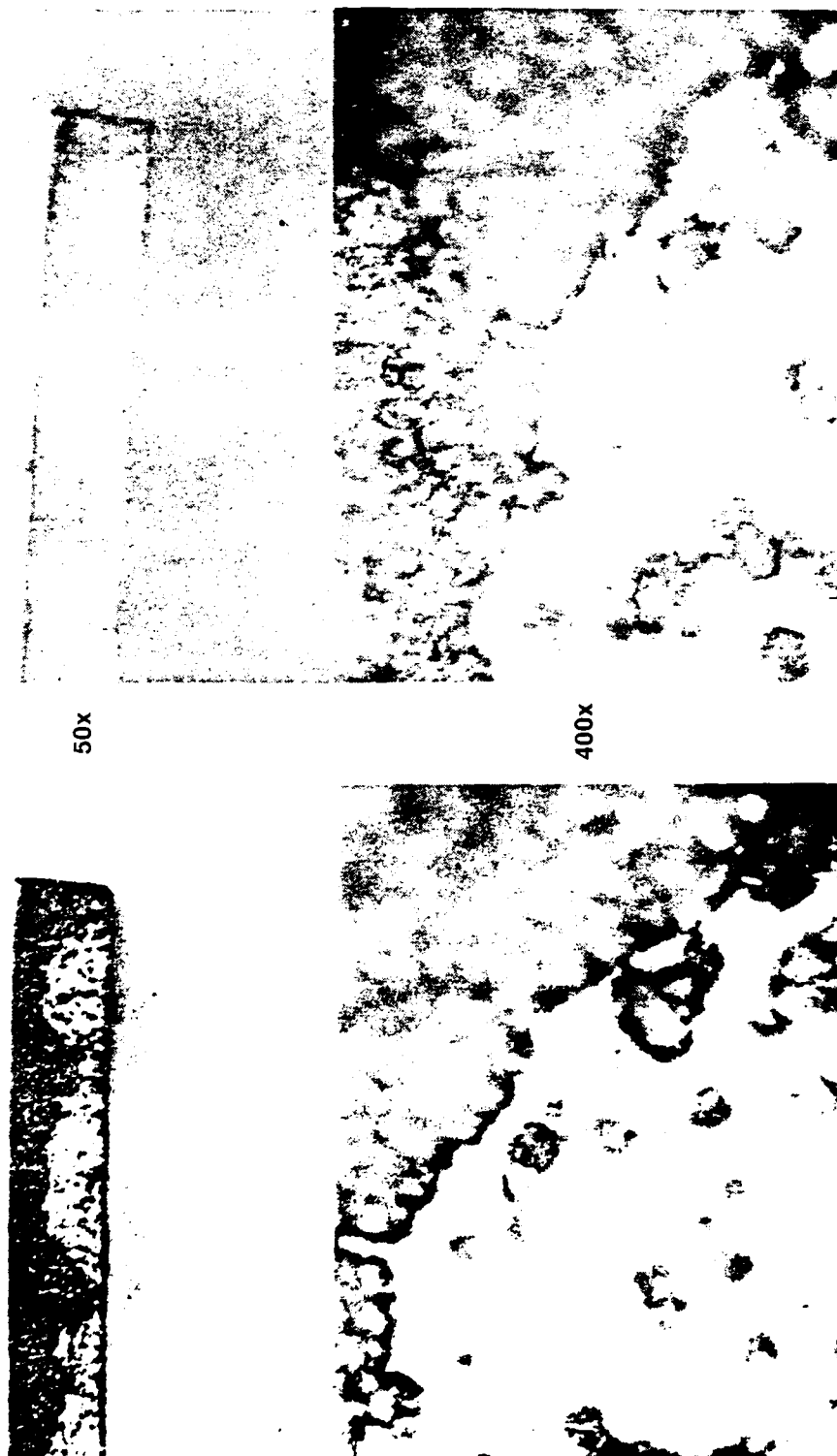
400X

After 100 Cycles



Pretest

Figure 54. Appearance of diamond film interface at edge of specimen 10-N-06-12,



50x

400x

After 100 Cycles

Pretest

Figure 55. Pretest appearance of diamond film interface at edge of specimen 10-N-96-14.

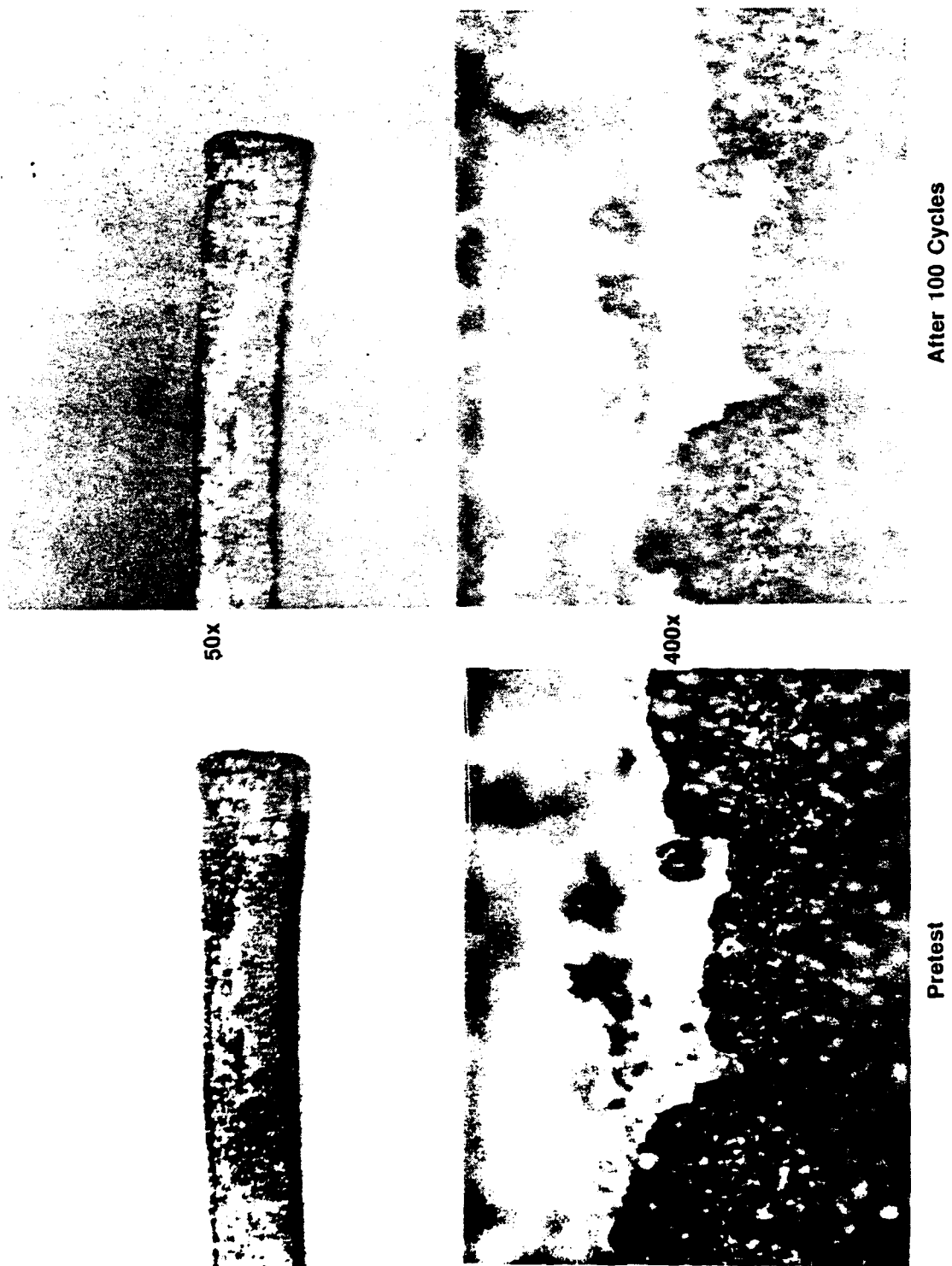


Figure 56. Appearance of diamond film interface at edge of specimen 10-N-06-15.

Sample Preparation--Diamond films were deposited on silicon wafers using microwave plasma-enhanced CVD. Silicon substrate material was subsequently etched away with HF/ NH_4OH , leaving free-standing diamond films. These films were then mounted with an adhesive to metal discs with apertures of varying sizes. Apertures were prepared by drilling holes and deburring the drilled edges. The test specimen assembly is shown in Figure 57. Figure 58 is a SEM of the film at 500X magnification.

Test Procedure--Mounted films were placed in a differential pressure testing apparatus. This apparatus consisted of five test chambers, each of which would accept one specimen. Specimens were supported on elastomer O-rings within each chamber. Each chamber is pressurized from a manifold fed by nitrogen gas. A regulator allowed variation of nitrogen supply to the manifold, producing variable differential pressure within each chamber. Pressure detection circuitry provided an indication of film rupture events. Film rupture was not subtle, and was easily detected by sudden onset of gas flow in the downstream gas exhaust line. The experimental setup is shown schematically in Figure 59. The four specimen assemblies are shown in Figure 60.

After sealing a specimen in its test chamber, differential pressure was slowly raised until film burst was observed, and nitrogen supply pressure was recorded. Specimens were removed from the test apparatus and disassembled for later SEM measurement of film thickness, required for calculation of tensile strength at rupture. Four measurements of film thickness were carried out on each specimen.

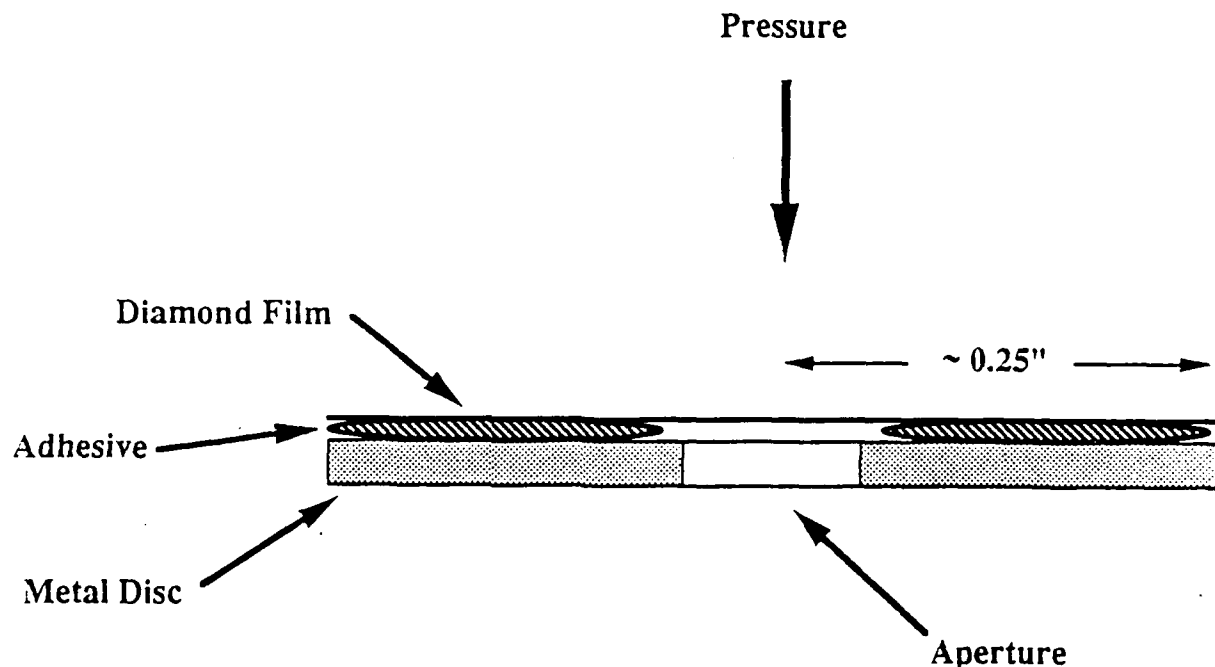


Figure 57. **Burst test specimen configuration.**

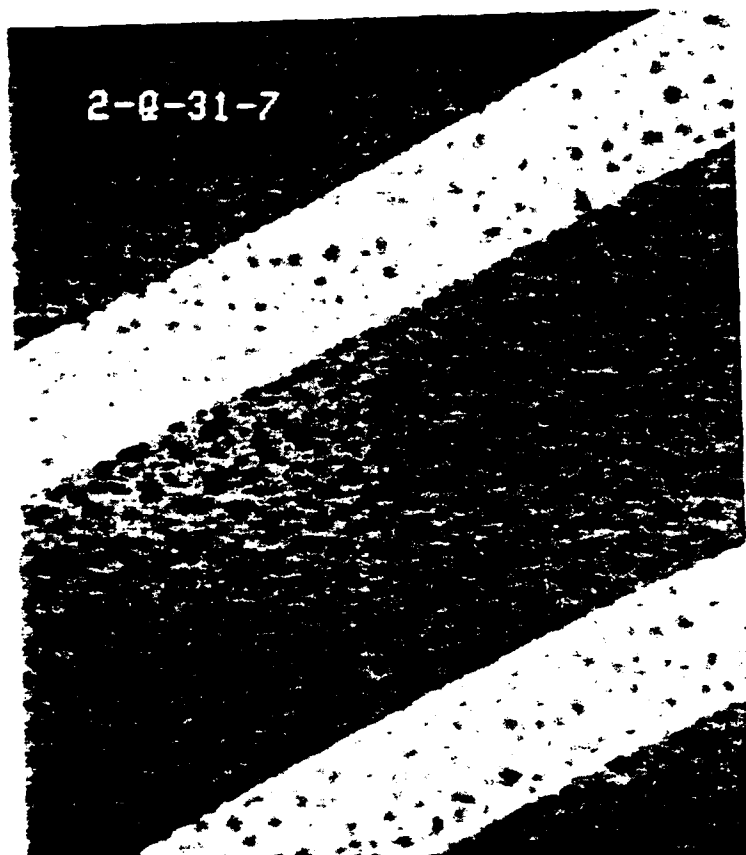


Figure 58. SEM of rupture specimen diamond film.

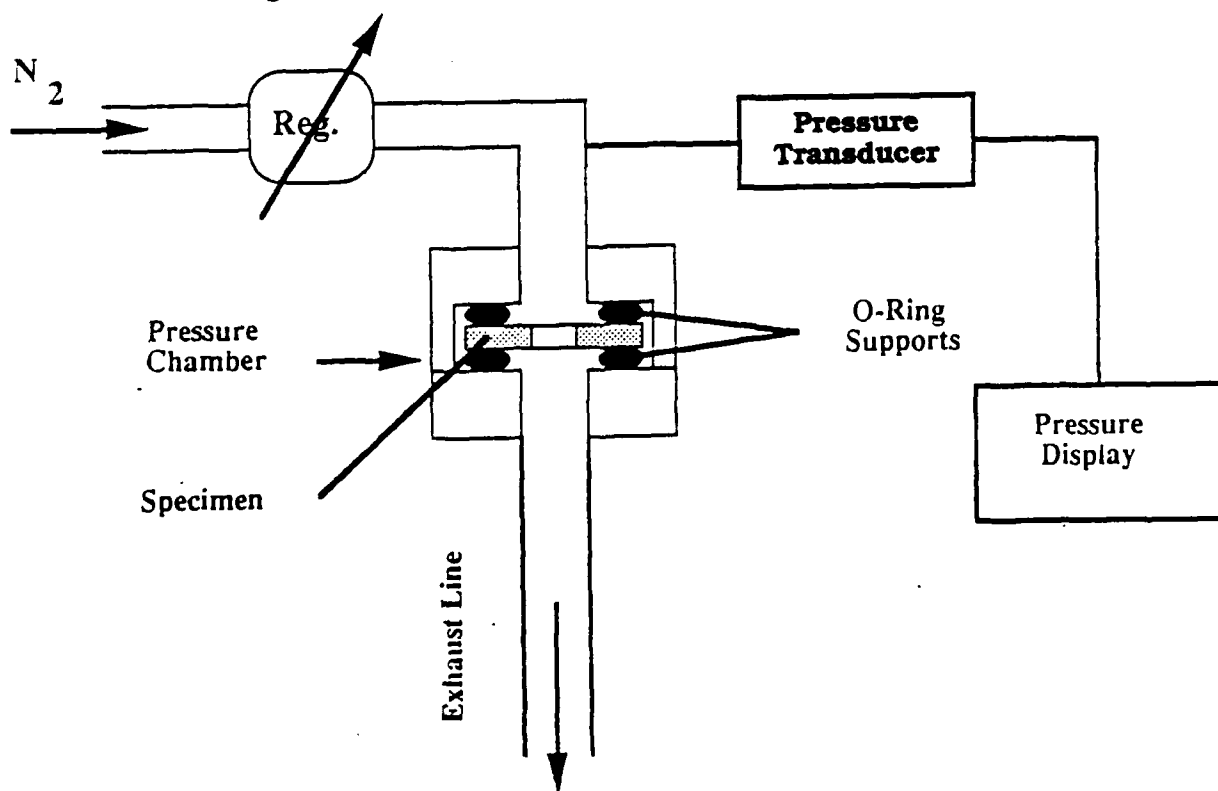


Figure 59. Burst test setup (schematic).

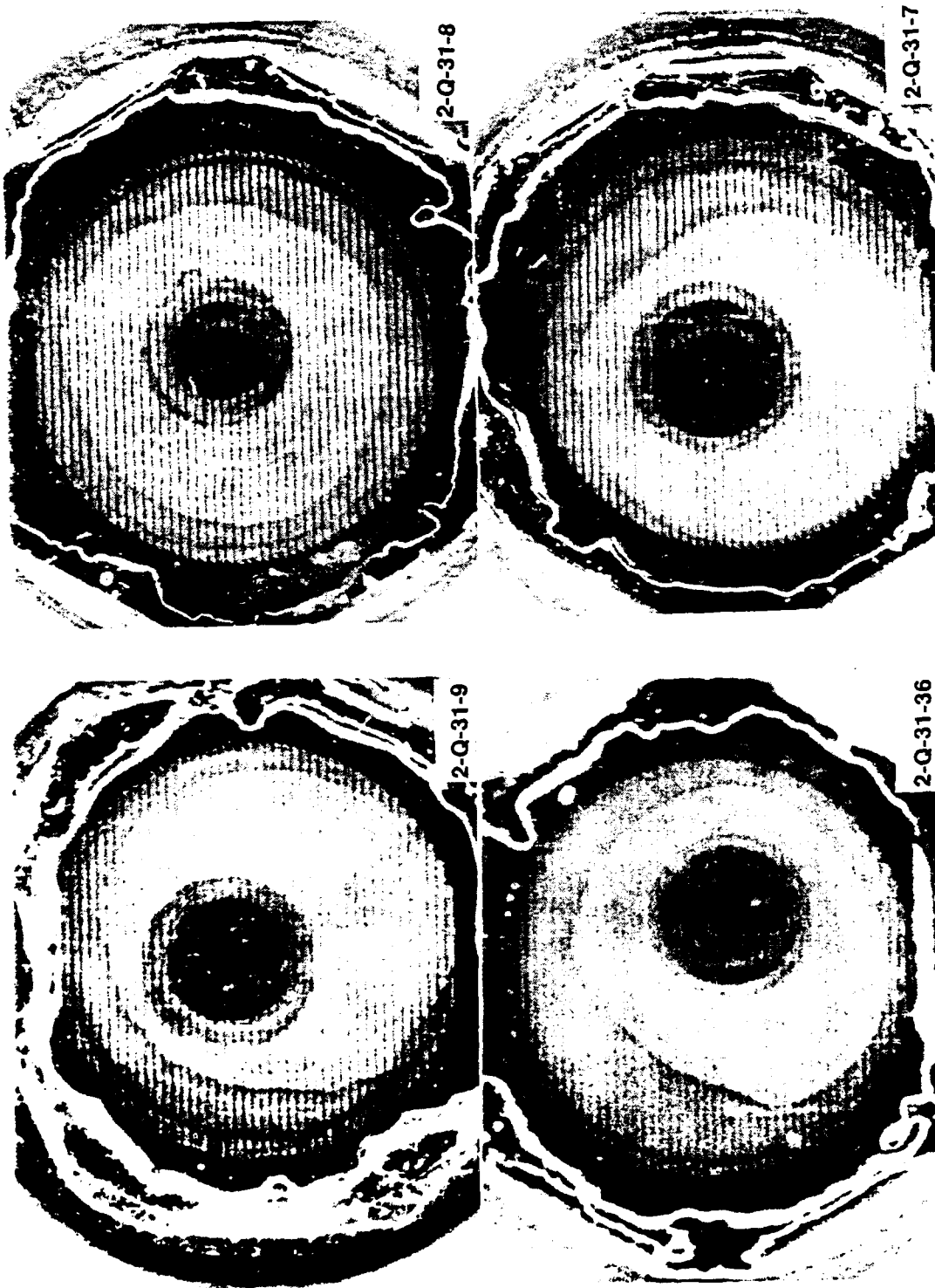


Figure 60. Rupture test specimens (10x magnification).

Several early attempts failed due to film fracture immediately on pressurization. Examination of test articles disclosed metal burrs left over from the aperture drilling operation, which probably punctured the film immediately on application of pressure. These trials were declared no-tests. Other specimens cracked during adhesive curing cycles due to adhesive shrinkage. Reduction of the amount of adhesive used and modification of the curing cycle eliminated this effect.

Characteristic film rupture pattern was rapid propagation of a crack around the aperture periphery, resulting in separation of a circle of diamond film from the test article. The burst event was rapid and unmistakable. Extensive fragmentation caused by subsequent impact with downstream portions of the apparatus precluded examination of the film debris in any meaningful way.

The data in Table 38 show stress at rupture for the four diamond films mounted on apertures and subjected to increasing differential pressure until failure. Also shown are film thicknesses as measured in the SEM and aperture size for each sample. These data are calculated using thick plate analysis, where:

$$S = (0.1875)P(D/t)^2,$$

in which

S = strength at rupture

P = differential pressure across film

D = diameter of orifice

t = film thickness

TABLE 38. Calculated Stress at Rupture (Thick Plate Model)

Film Thickness, microns (+/- σ)	Aperture Diameter, inches	Burst Pressure, psi	Stress at Rupture, psi
17.1 +/- 1.7	0.06	54	75,300
16.8 +/- 1.0	0.06	90	140,000
11.1 +/- 0.6	0.157	48	1,117,200
13.4 +/- 0.8	0.10	42	281,900

Selection of thick plate or membrane analysis must be made on the basis of expected deflection of the film under test conditions. If deflection is greater than $\sim 1/2$ film thickness, membrane analysis is required.

Deflection can be calculated from the following relationship:

$$(Wa^4)/(Et^4) = \{16/[3(1-v^2)]\} \cdot [(y/t) + 0.488(y/t)^3]$$

where

W = differential pressure

a = radius

E = Young's modulus for diamond, $\sim 152 \times 10^6$

v = Poisson's ratio for diamond, ~ 0.2

y = deflection

t = thickness

In reduced form, $y^3 + ay + b = 0$

of which the root $y - a + b$ is selected.

(Complex roots of the form $-[(a+b)/2] + /-[(a-b)/2] \cdot (-3)^{1/2}$ are rejected.)

In all cases, it was found that $y > t/2$, indicating that membrane stress analysis is the applicable model. Calculated deflections and stresses are shown in Table 39.

TABLE 39. Calculated Stress at Rupture (Membrane Model)

Film Thickness, inches	Deflection, inches	Stress at Edge, psi	Stress at Center, psi
6.95×10^{-4}	1.16×10^{-3}	708,000	611,000
6.59×10^{-4}	1.13×10^{-3}	653,000	567,000
4.35×10^{-4}	2.22×10^{-3}	163,000	188,000
5.29×10^{-4}	1.24×10^{-3}	221,000	206,000

The analysis above indicates that, contrary to earlier work, the tensile stress at rupture for CVD diamond films is not significantly different than that reported for single-crystal natural diamond specimens, as discussed in Appendix B. As shown in the following graphs, Figures 61 and 62, there is a very large difference in calculated stresses resulting from selection of analytic model. Furthermore, substantial scatter in the data should caution against attributing high accuracy to these data. The limited number of data points covers a range from 163,000 to 708,000 psi, with the average for the four measurements being 436,000. The most likely value is that of natural diamond, or about 500,000 psi. Perhaps the only trend of note is the increase in tensile stress at rupture, as indicated by membrane analysis, as film thickness increases above 16 microns. More work is required to determine whether this is a real effect.

5.5 PROPELLANT CORROSION RESISTANCE

Free-standing samples of diamond film were prepared at Crystallume by deposition on a silicon substrate, followed by etching away of the silicon. These samples were provided to the Astronautics Laboratory (AFSC) for propellant corrosion studies. No detectable effects on the film were seen in vapor of ClF_3 , or N_2O_4 at 170 F, nor in liquid N_2O_4 or N_2H_4 at 65 F. A report of this study is given in Appendix E.

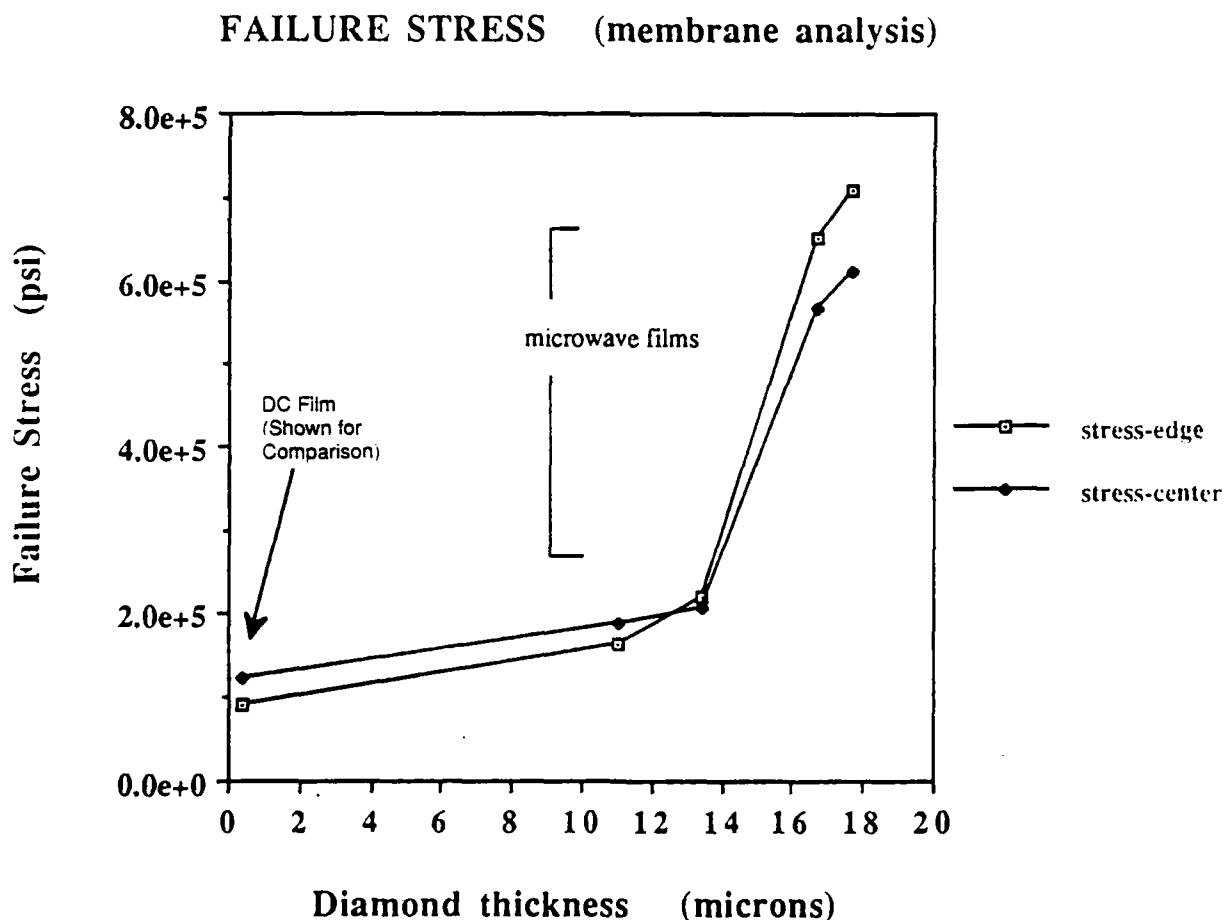


Figure 61. Calculated stress at failure.

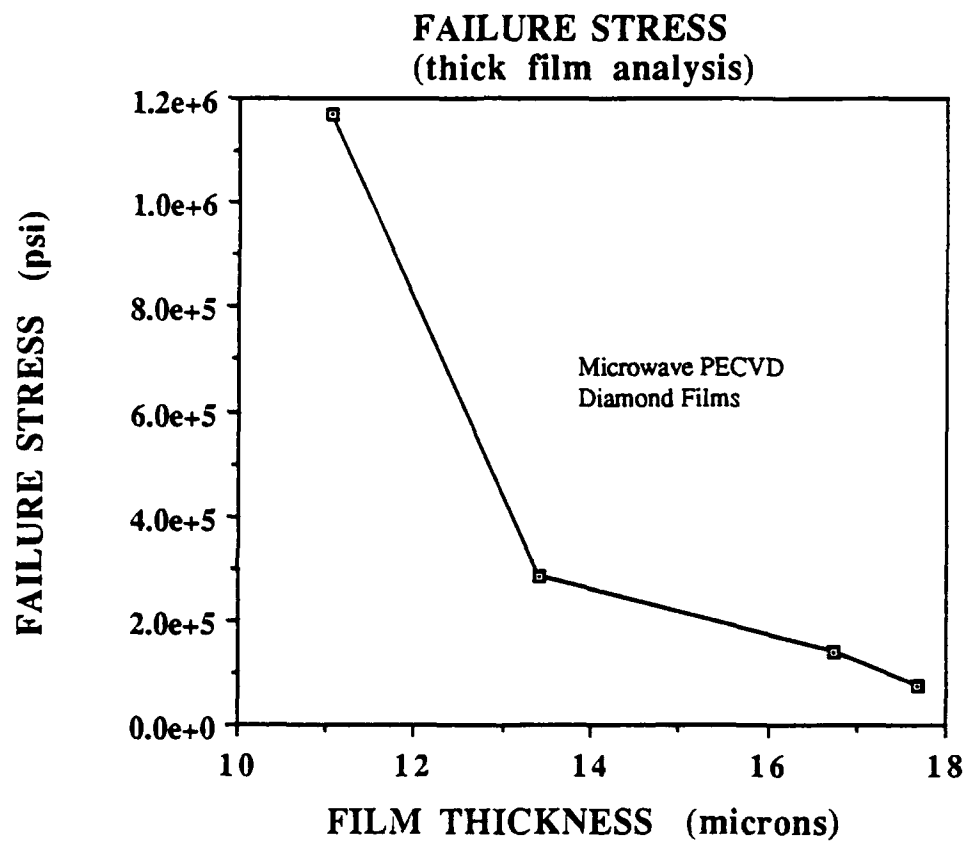


Figure 62. Failure stress versus film thickness calculation using thick failure analysis.

6.0 APPLICATIONS ASSESSMENT AND DEVELOPMENT PLANNING

The broad categories of aerospace applications have been discussed in Section 4. Initial application assessment to reduce the potential applications to a few high-value items is also covered there.

Applications which have been considered for further study after the initial screening are: (1) bearings for rotating machinery, (2) pressure vessel monolithic structures, (3) composite structures, and (4) hydrogen barriers. After further review, the use of diamond film for bearings was chosen for further study. A technology development plan has been prepared for the bearing application, which is discussed in Section 6.2. Some aspects of the application of diamond film to bearings are discussed below.

6.1 APPLICATION OF DIAMOND FILM FOR BEARING SURFACES

The attractive properties of diamond film make it an excellent choice for applying to bearing and sealing surfaces. Its high hardness, high thermal conductivity, low coefficient of friction, and high modulus are ideal characteristics for bearing or sealing surfaces. In addition, this technology is applicable to gears, splines, clevis pins, and other highly loaded contact surfaces.

Bearings are of either contact type, with ball or roller elements, or are noncontact, hydrodynamic or hydrostatic film bearings. Even the latter type can involve metal-to-metal contact during starting, shutdown, or transient overload. The bearing structures are characterized by repetitive high cycle stresses, which result in limited life. Specialized lubricants and surface treatments are used to extend the operating capability of bearing systems. In many rocket propellant applications, the bearing fluid is a propellant which is not a good lubricant. Some rocket turbopump bearing experience is listed in Table II of Ref. 25.

Bearings are characterized as to their life, load capability, and DN or product of speed and diameter. Life of a bearing installation of conservative design is a function of high cycle fatigue from repeated stresses. In this, the failure history of a group of bearings gives a statistical life distribution. The "B-10" life designation is that life exceeded by 90% of the bearings. This life, L , varies inversely as load, W , for a given bearing design, as $L_2/L_1 = (W_1/W_2)^n$, where n is a value close to 3 for a typical point contact roller bearing.

The speed and diameter limits, DN , are a general measure of maximum speed capability for a given bearing design. Some typical values are shown in Table 40 from Ref. 25. At the extreme values of DN , all aspects of the bearing design fabrication and assembly must be carefully controlled or failure will result.

The properties of diamond which determine its use as a bearing material are:

- o Hardness
- o Coefficient of friction
- o Modulus of elasticity
- o Thermal conductivity
- o And, when used as a coating, adherence

TABLE 40. Speed Limits for Bearings

Bearing Type	Existing Max	Existing Max	Limiting Factor	Test Coolant
	Turbopump, DN, million, mm-rpm	Test, DN, million, mm-rpm		
Conrad-Type Ball	1.6	1.6	Cage weakness	Liquid hydrogen
Angular- Contact Ball	2.05	3.0	Heat generation	Liquid hydrogen
Cylindrical Roller	1.6	1.6	Roller guidance, cage slippage	RP-1

These parameters control wear, fatigue failure, and therefore determine the maximum load and DN achievable for a given bearing type.

Bearing Wear--Wear mechanisms can be classified as:

- o Abrasive
- o Corrosive
- o Galling (adhesion)
- o Surface fatigue

Resistance to abrasive wear was found by Kruochuv, Ref. 26, to be directly related to hardness, as shown in Figure 63, which has been extrapolated to include diamond. Figure 64 shows the effect of material hardness on bearing life using an empirical method developed for rolling-element steel bearings. The dynamic capacity of the bearing is related to Rockwell hardness by

$$C_2 = C_1 \left(\frac{R}{58} \right)^{3.6} \text{ where}$$

C_1 is the dynamic capacity at Rockwell Hardness of 58 (where dynamic capacity is the allowable dynamic bearing load in pounds).

C_2 is the dynamic capacity at R_c hardness.

$$L_2 = L_1 \left(\frac{C}{C_2} \right)^3, \text{ or}$$

$$L_2 = L_1 \left[\frac{1}{\left(\frac{R}{58} \right)^{3.6}} \right]^3$$

As seen from the figure, increasing the Rockwell hardness from 30 to 58 results in a 10-fold increase in the life of steel bearings.

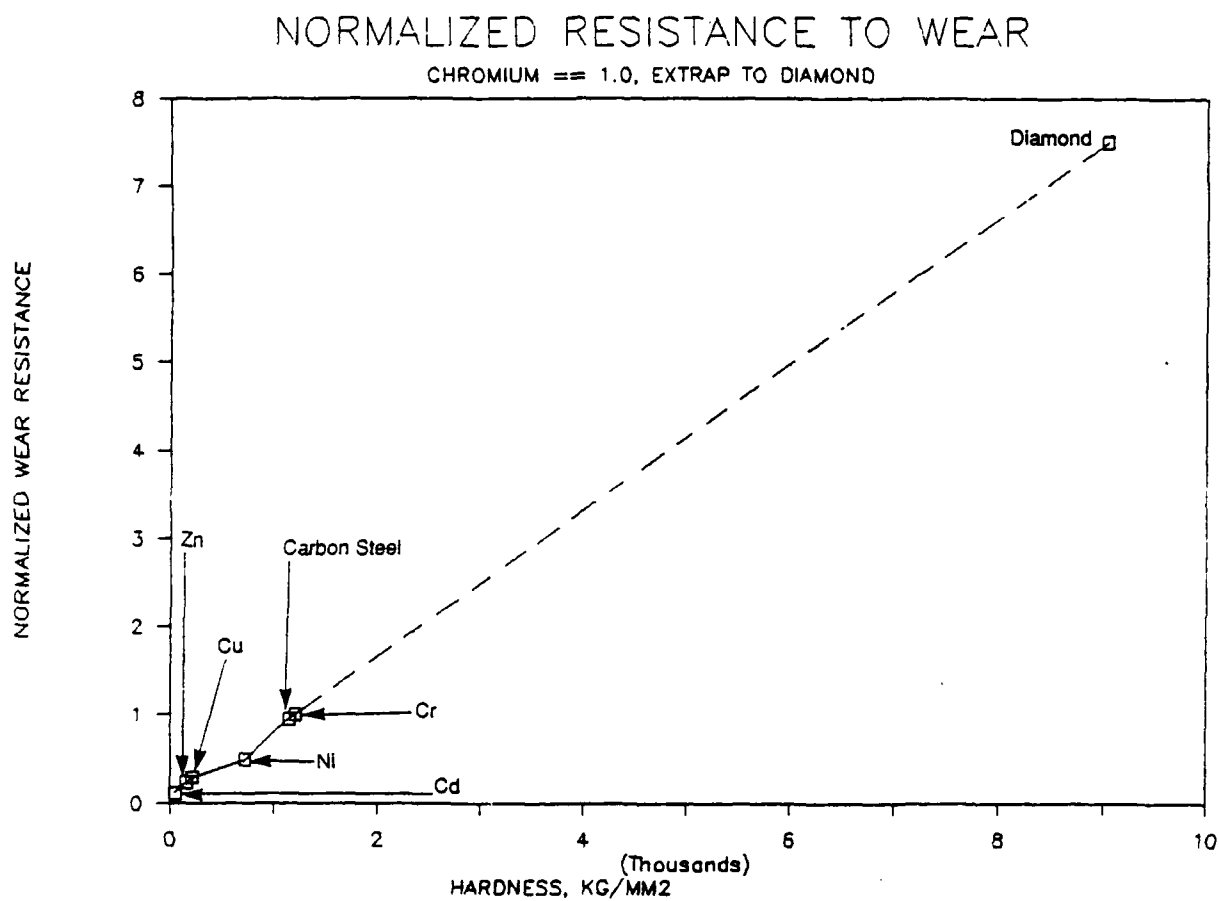


Figure 63. Normalizer resistance to wear chromium = 1.0, extrapolated to diamond.

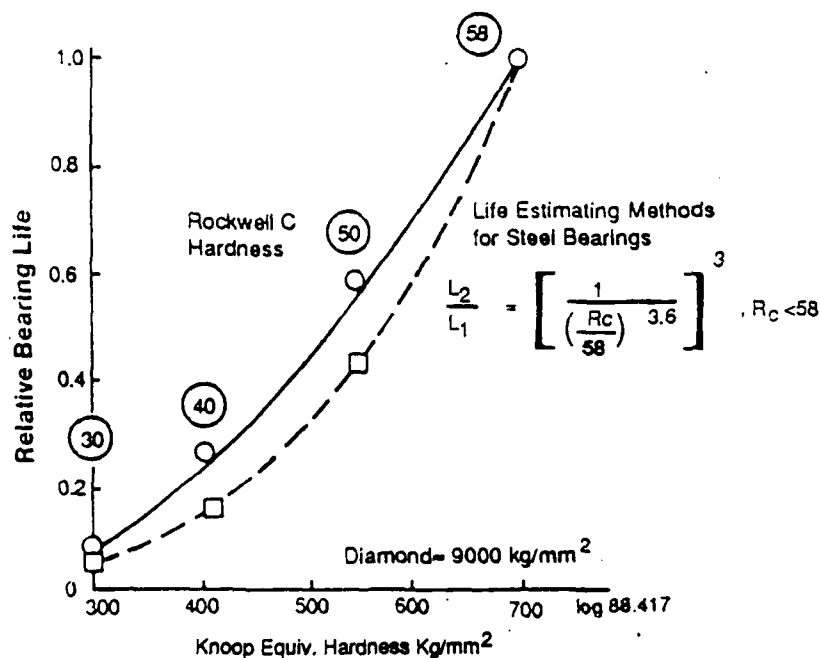


Figure 64. Effect of surface hardness of bearing life.

Diamond is too hard to be measured on the Rockwell hardness scale and, thus, comparisons can only be made by using the Knoop equivalent values. The hardness of steel bearings is in the range of 5.9 to 7.8 GPa (600 to 800 kg/mm², 0.8 to 1.1x10⁶ psi) on the Knoop scale. Diamond films are estimated to have a hardness of approximately 88.2 GPa (9000 kg/mm², 12.8x10⁶ psi) at room temperature. When looking at the curve of Figure 64, it is apparent that a major life enhancement might be expected, but the magnitude is uncertain.

Since no direct comparison can be made for the relative life of diamond vs. steel bearings using the empirical methods, a more theoretical approach is shown in Figure 65, based on data from Ref. 27. This analysis is based on a thin-film-lubricated rolling contact bearing. In this case, the hardness of diamond is projected to reduce the surface wear rate by one to two orders of magnitude.

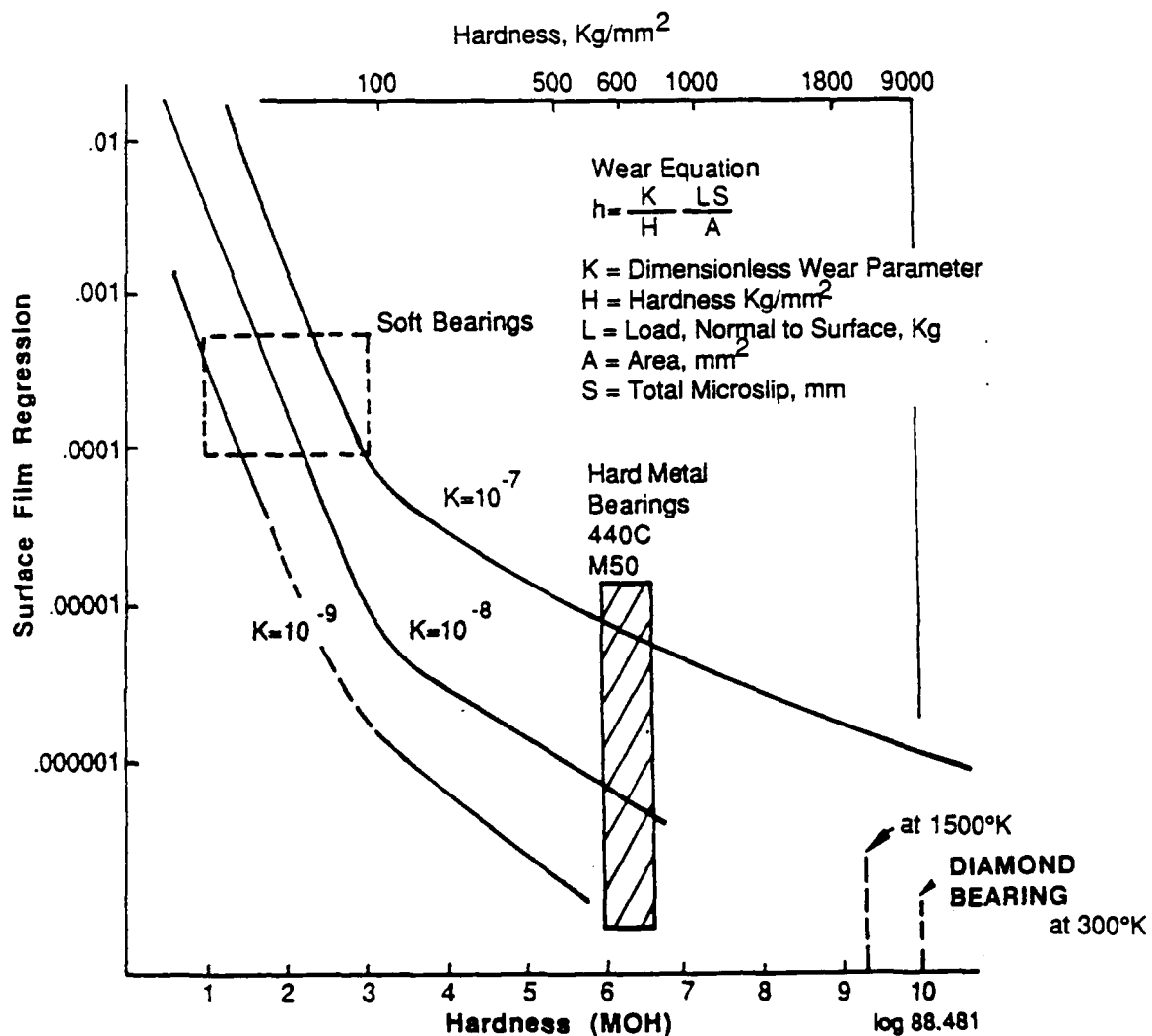


Figure 65. Wear rates for rolling contact bearings on thin film lubricated bearings.

A second benefit of using the diamond film results from the fact that diamond retains very high values of hardness at elevated temperatures where steel alloys can no longer be employed. This is illustrated in Figure 66, which shows the effect of temperature on the hardness of diamond and the hardness of a typical steel bearing material. The much improved high-temperature hardness of diamond relative to steel could reduce the cooling requirements for bearings and/or provide increased design margin against failure of a bearing cooling system.

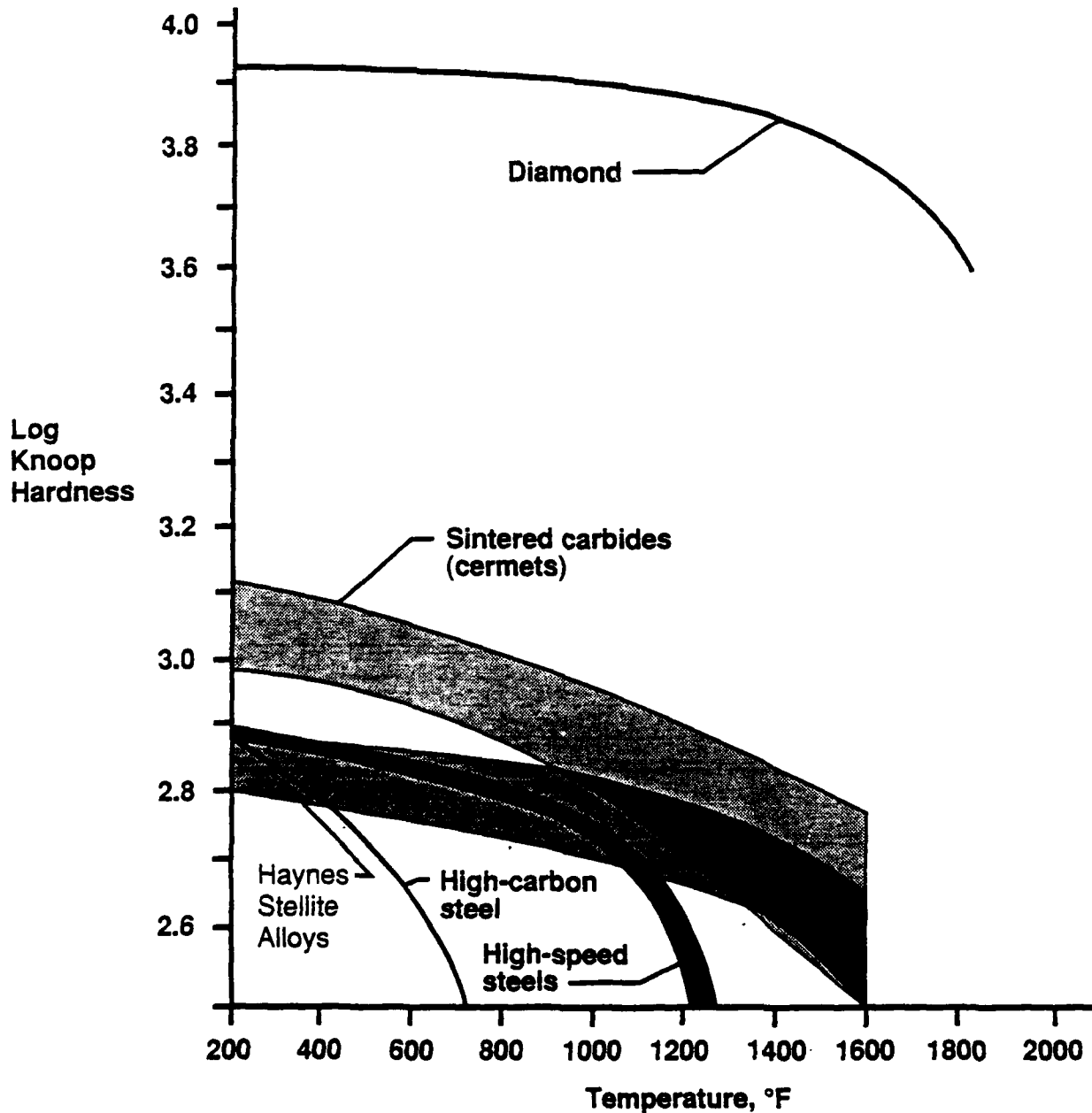


Figure 66. Hardness vs function of temperature for different classes of bearing materials.

The effect of elastic modulus on wear is in Figure 67, from Ref. 28, extrapolated to show diamond. Hardness or elasticity data were correlated in Ref. 29 as a function of the ratio of hardness to elastic modulus. The resulting ordering of materials generally matches their resistance to wear, but there are some inconsistencies. A better correlation with wear is given by the product of hardness and elastic modulus. This product is given in Table 41 for a wide range of materials, ordered by decreasing ExH. This ordering better matches the resistance to wear of the materials (e.g., tungsten carbide ranks above gray iron and chromium plate) than does the ranking by H/E of Ref. 29, also shown in the table.

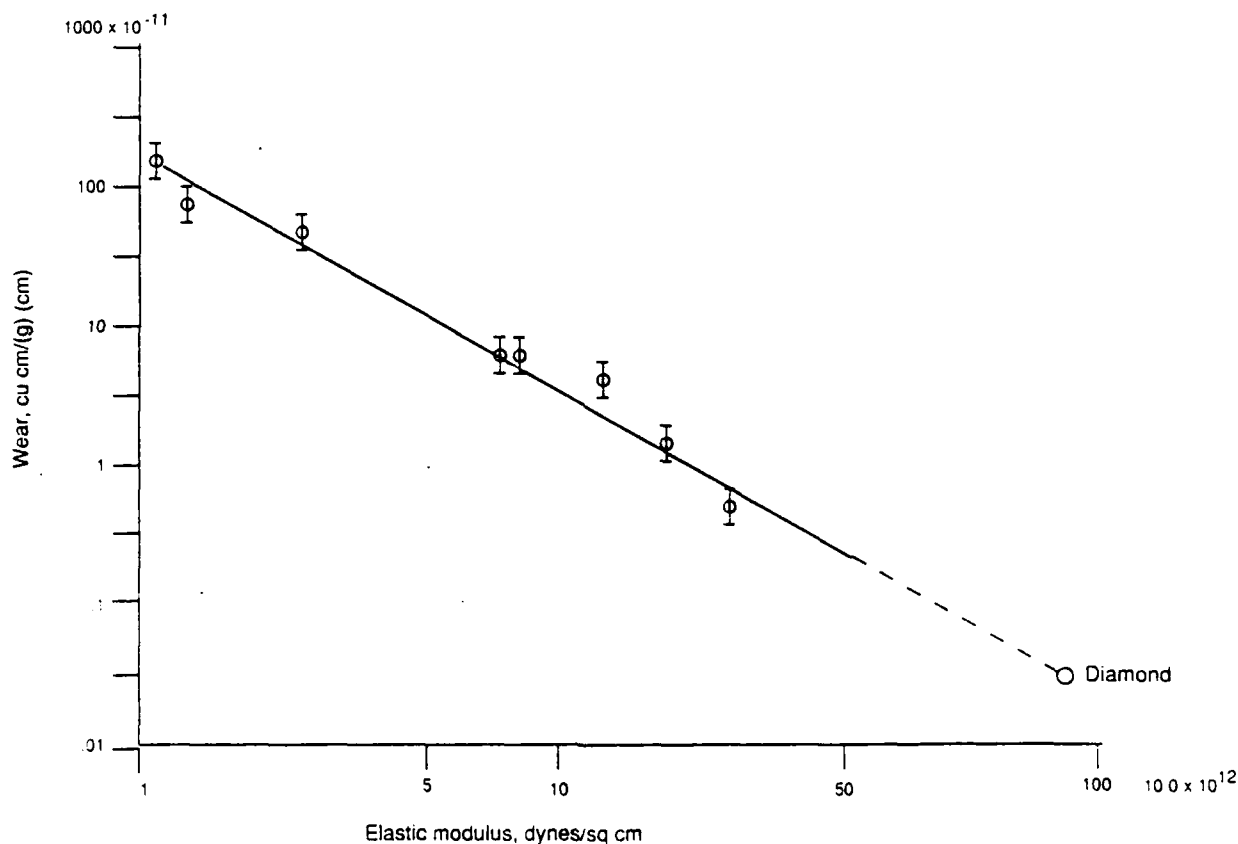


Figure 67. Wear versus elastic modulus.

TABLE 41. Ratio of Hardness to Modulus of Elasticity for Various Materials

Material	Condition	Modulus of Elasticity, E, psi	Brinell Hardness Number, H	Hardness Number x Elas. Modulus, Millions of psi	Hardness Number/ Elas. Modulus, H/E (Millions of psi) ⁻¹
Diamond	CVD	150	10,000	1,500,000	67
Tungsten Carbide	9% Cobalt	81	1,800	145,000	22
Alumina (Al ₂ O ₃)	Bonded	15	2,000	30,000	143
Steel	Hard	29	600	17,400	21
Chromium Plate	Bright	12	1,000	12,000	83
Gray Iron	Hard	15	500	7,500	33
Titanium	Hard	17.5	300	5,250	17
Structural Steel	Soft	30	150	4,500	5
Chromium Metal	As Cast	36	125	4,500	3.5
Malleable Iron	Soft	25	125	3,125	5
Wrought Iron	Soft	29	100	2,900	3.5
Gray Iron	As Cast	15	150	2,250	10
Aluminum Alloy	Hard	10.5	120	1,260	11
Copper	Soft	16	40	640	2.5
Silver	Pure	11	25	275	2.3
Aluminum	Pure	10	20	200	2
Tin	Pure	6	4	24	0.7
Lead	Pure	2	4	8	2

Corrosion resistance is important for bearing life; in particular, for bearings exposed to propellant or operating at high temperatures. Diamond is compared to conventional corrosion-resistant materials for race and rolling elements in Table 42 from Ref. 25. Diamond is much harder than the materials used for high-temperature corrosion resistance, as shown in Figure 66; however, high-temperature hardness data for CVD diamond film must be developed.

The effects of exposure to low pressure on friction coefficient must be understood for bearings used in some space applications. The large increase in friction coefficient of graphite surface due to loss of absorbed surface water has been well documented. The nonlinear effect of low pressure on a commonly used bearing steel is shown in Figure 68 from Ref. 29.

TABLE 42. Corrosion-Resistant Race and Rolling Element Materials

Temperature Range, °F	Designation	Hardening	Disadvantages
TBD	Diamond	CVD	TBD
-423 to 700	440-C	Through	Brittleness; not completely corrosion resistant
-423 to 1200	Haynes 25	Work hardened	Low hardness; limited availability; high cost
-423 to TBD	Stellite Star-J	Cast Chill cast	Lack of test experience; high cost
	Stellite 19	Cast Chill cast	Low hardness
	Stellite 3	Cast Chill cast	Low hardness
-423 to TBD	Titanium Carbide K162B	Through	Brittleness; high modulus resulting in high stresses; high cost; difficult to fabricate
-423 to TBD	Tungsten Carbide	Through	Brittleness; high modulus; heavier than steel

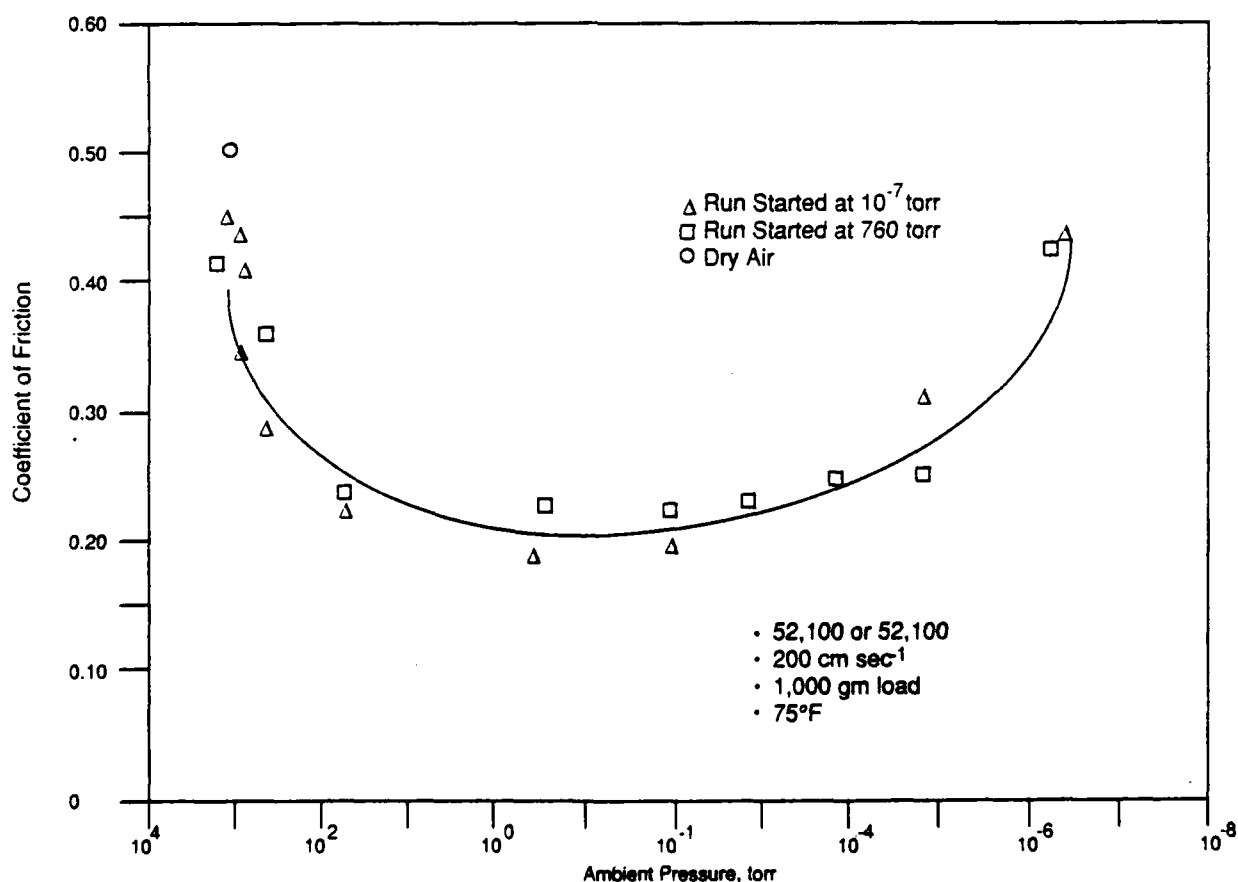


Figure 68. Effect of ambient pressure on coefficient friction.

As can be seen from these preliminary analyses, using diamond films as coatings on bearings can result in large payoffs in life and extension in operating conditions.

Benefits

(1) Advanced Launch System

The Advanced Launch System, ALS, will have high-pressure hydrogen turbopumps. Initial design studies show that titanium alloy is the material of choice for the impeller because of its high strength-to-weight ratio. Any other material requires a more complex pump design, with more stages. Titanium 5Al2.5V is the alloy of choice because of its high ductility at liquid hydrogen temperature (approximately 10%).

Labyrinth seals on the impeller are problem areas with the titanium alloy because they operate at elevated temperature and fail rapidly from hydriding. These surfaces in ALS can be diamond coated. This would reduce frictional heating and provide a barrier to hydrogen attack.

Other bearing and seal surfaces in ALS can benefit from diamond coating to reduce friction and increase life. Although the ALS will be a single-use vehicle, it must operate for several test cycles leading up to flight. Therefore, its turbopump components will have been exposed to hydrogen and will be subject to hydrogen embrittlement.

(2) Titan

The Titan engine system is being improved to provide greater lift capability. This involves increased pressure and thrust, larger propellant tanks, and longer burns. Although the present system is capable of providing the required upgrade, it is accompanied by a reduced design margin. Life endurance testing has indicated gearbox overheating and tooth wear and fretting of a spline in an aluminum pump impeller and could benefit from a hard, low-friction surface coating such as would be provided by diamond film. A similar situation probably exists for an uprated RL-10 engine which uses a gear drive system.

(3) XLR-132

The XLR-132 engine incorporates a high-modulus TZM (molybdenum) alloy shaft which includes labyrinth seals which are one of the life-limiting parameters. Attempts to improve design life margin by hard Cr plating have been unsuccessful because Cr will not adhere to the shaft material. In contrast, diamond-molybdenum bonds have been reported to be outstandingly good. The life of the (WTiC), K5H alloy balls and BG42 race material employed in the XLR-132 may also be enhanced by the addition of a diamond film.

(4) SSME

The SSME turbopump bearings represent the greatest single propulsion system bearing life improvement effort, as measured by total funds being expended and the number of independent investigations. A number of these design fixes involve the application of thin, hard surfaces over the existing bearing material substrate (AMS 5618). This material was originally selected for its high strength, high hardness, R_C 58-62 (735 Knoop), and corrosion resistance. These metallic materials, however, do not come close to meeting the 55-mission life requirement.

Ng and Naerheim, Ref. 30, of Rocketdyne and the Rockwell Science Center reported significant life improvement when RF sputtered TiN (Knoop hardness, 1800 Kg/mm²) is applied to the wear surfaces.

Thom and Dolan, Ref. 31, of the NASA/Marshall Space Flight Center reported a 300% bearing life improvement in simulation testing when 1/2 micron of zirconium nitride (Knoop hardness 1500) is applied to the bearing surface. Their test method and resulting data are displayed in Figure 69. Wedeven and Miller, Ref. 32, working for SKF Aerospace, reported similar benefits for TiN and hard chrome plating and even better life improvement (500 to 1000%) for Si₃N₄ (Knoop hardness 2200) in similar tests.

The hardness of diamond (Knoop 9000 Kg/mm²) offers substantial reward if hardness is the primary measure of life improvement. Other desirable factors which come into play are high thermal conductivity, low friction coefficient, and high elastic modulus. In this respect, the properties of diamond film are all superior to the nitride compounds.

(5) Other Liquid Rocket Applications

XLR-134 and OTV turbopump assemblies operate with H₂ and O₂ cooled bearings for which life testing is presently in progress. These designs are also prototype to the NASP TPAs. Each requires demonstration of a 20-hr life. The XLR-134 uses rolling contact bearings, while the OTV uses hydrostatic thrust and journal bearings. Numerous highly stressed wear surfaces in each application could be considered for use of diamond film coating to increase design margin.

Limiting Use Factors--In all of the identified applications, a low coefficient of friction, combined with hardness to resist wear, high thermal conductance to remove local hot spots, and a high modulus to resist deformation are required. The friction coefficient, however, is not an entirely invariant property of the material, but is dependent on the operating environment and exposure history as adsorbed surface films contribute to the sliding action.

The influence of propellants on the friction and propellant compatibility must be established before diamond films can be considered as suitable for applications where low friction is essential. The propellants of interest are as follows:

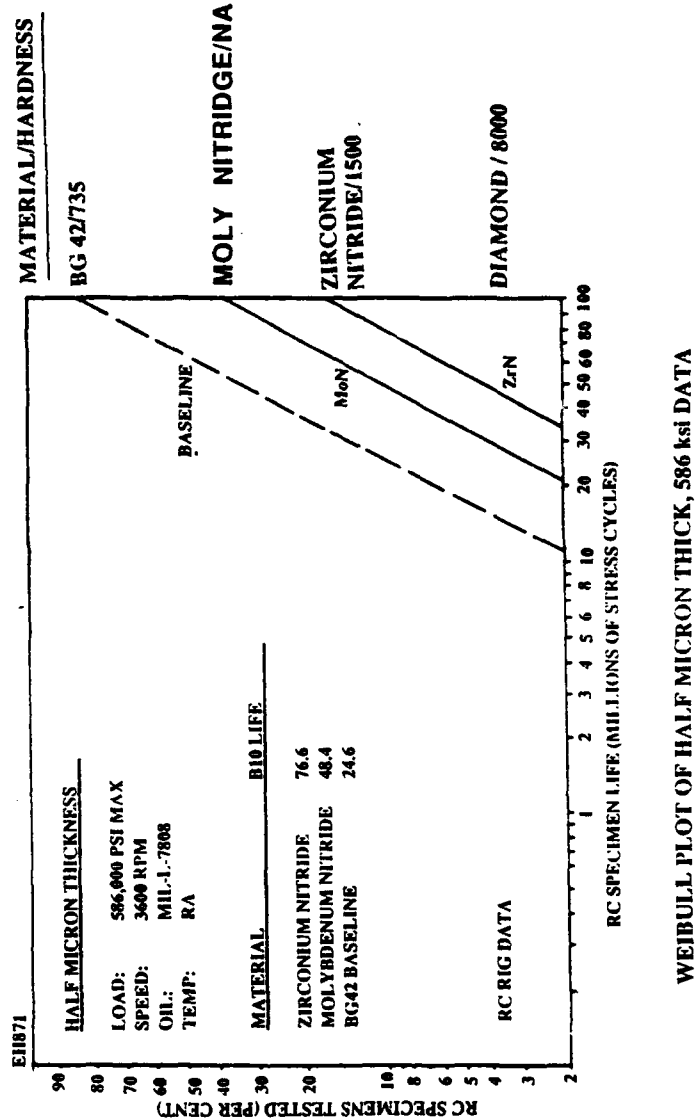
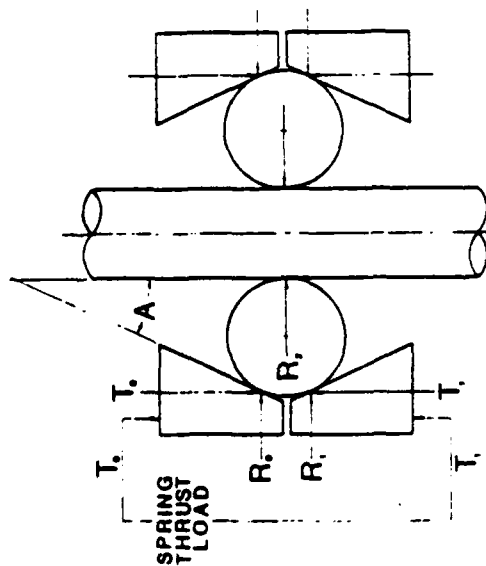
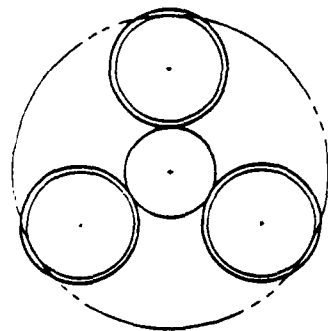


Figure 69. NASA-MSFC bearing life tester.

- o Fuels Liquid and gaseous hydrogen
Liquid and gaseous methane
MMH, N₂H₄, A-50 (storable propellants)
- o Oxidizers Liquid and gaseous oxygen
N₂O₄ (storable oxidizer)
ClF₃ and ClF₅

A second factor is that the deposition temperature for the diamond film is 600 to 800°C, while the strength and hardness properties of the substrate metal are reduced above about 260°C for 440C alloys, and 550°C for BG42 alloys.

6.2 TECHNOLOGY DEVELOPMENT PLANNING

Technology demonstration of practical use of diamond films in aerospace applications will assist in rapid utilization of this new material. A program for demonstration of diamond films for turbopump bearings is described in Section 6.3.2. However, before such a program is undertaken, a better understanding is required of the properties of diamond film and their correlation with process variables. For this reason, the technology demonstration should be preceded by a more basic activity which would be an extension of the preliminary characterization measurements made during Phase III of this program. The estimated resources for this activity are the equivalent of 1.5 person-year.

6.2.1 Properties Determination for CVD Diamond--Most engineering properties of CVD diamond should be experimentally confirmed, rather than relying on natural diamond data or isolated measurements of films prepared under a variety of incompletely defined conditions.

To have confidence in properties whose values are critical to an engineering application, sufficient measurements must be made to assure statistical confidence and process repeatability. In addition, the effects of major process variables should be isolated both to allow intelligent process control and to permit optimization of film characteristics.

The properties of primary interest are shown in Table 43, which is a subset of the properties data table, showing those 14 parameters of primary interest. The list is still extensive and includes some measurements (chemical reactivity, mechanical adherence, diffusion coefficient, thermal stability) which would require extensive multiparameter programs for proper study.

If the list is held to those parameters necessary for bearing design, and if the bearing environment is defined, the number of measurements becomes more manageable. The parameters of primary interest are shown in Table 44.

TABLE 43. Diamond Film Properties of Primary Interest

DIAMOND FILM PROPERTIES OF PRIMARY INTEREST

CLASS	PROPERTY	UNITS	VALUE
Chemical	Reactivity		
Electronic	Breakdown field		5.58
Electronic	Dielectric constant	--	10E12--10E16
Electronic	Resistivity, Ib	Ohm-cm	10E4--10E12
Electronic	Resistivity, IIa	Ohm-cm	10-10E3
Electronic	Resistivity, IIb	Ohm-cm	
Mechanical	Adherence	dynes/cm2	
Mechanical	Compressibility	cm2/dyne	2.3x10E-13
Mechanical	Compressive strength	dynes/cm2	9.65x10E11
Mechanical	Friction coefficient, dynamic		
Mechanical	Friction coefficient, static		
Mechanical	Hardness	Kg/mm2	>9000
Mechanical	Shear strength	dynes/cm2	
Mechanical	Tensile strength	dynes/cm2	3.45x10E10
Mechanical	Wear rate		
Mechanical	Young's Modulus	dynes/cm2	10.35x10E12
Optical	IR transmission		
Optical	Refractive index (2589.3nm)	--	2.417
Optical	UV transmission		
Optical	Visible transmission		
Physical	Density	gm/cm3	3.515
Physical	Diffusion coefficient	cm2/sec	6.4x10E-12
Thermal	Conductivity @25C	Watt cm-1 C-1	20
Thermal	Expansion coefficient		
Thermal	Linear expansion, @400C	cm cm-1 C-1	3.5x10E-6
Thermal	Linear expansion, @750C	cm cm-1 C-1	4.5x10E-6
Thermal	Linear expansion, @78C	cm cm-1 C-1	1.5x10E-6
Thermal	Specific heat @150K	cal mol-1 deg C-1	0.24
Thermal	Specific heat @289K	cal mol-1 deg C-1	1.46
Thermal	Specific heat @400K	cal mol-1 deg C-1	2.52
Thermal	Stability, onset of oxidation in air	C	600
Thermal	Stability, onset of graphitization in vacuum	C	1400-1700

TABLE 44. Diamond Properties of Primary Interest

Parameter	Preliminary Measurements Made In Phase III	Comment
Chemical reactivity	x	Environment dependent
Mechanical adherence	x	Substrate dependent
Compressive strength		
Tensile strength	x	
Young's modulus		
Friction coefficient		Environment dependent
Hardness	x	
Wear rate		Environment dependent
Diffusion coefficient	x	Environment dependent
Thermal coefficient of expansion		
Thermal conductivity		

Initial measurements have been made of six of these values during this program. However, much more is required to provide reliable data with high confidence.

Figure 70 outlines a one-year program in which to make these measurements. During Task 1, the specific measurements and environments would be finalized, as would the deposition process type and standard operating conditions.

Task 2 involves continual sample preparation over a four-month period. Process variables will be adjusted based on the results of the specimen preparation and properties measurement.

Laboratory measurement of physical properties will be made during Task 3. Each type of measurement will be made on small lots (approximately twelve specimens) so that the results can be fed back to the processing for control and optimization of operating conditions. Three iterations of the more important process/measurements are planned. Table 45 shows a plan for properties determination.

Specific measurements would be selected from this list during Task 1, using the following criteria:

(1) Criticality of the measurement to high-value, near-term Air Force application (i.e., TPA bearings).

(2) Degree of uncertainty in the value of the property.

(3) Resources required to make the measurement. The need to limit resource requirements precluded expensive test procedures, such as all-up bearing friction

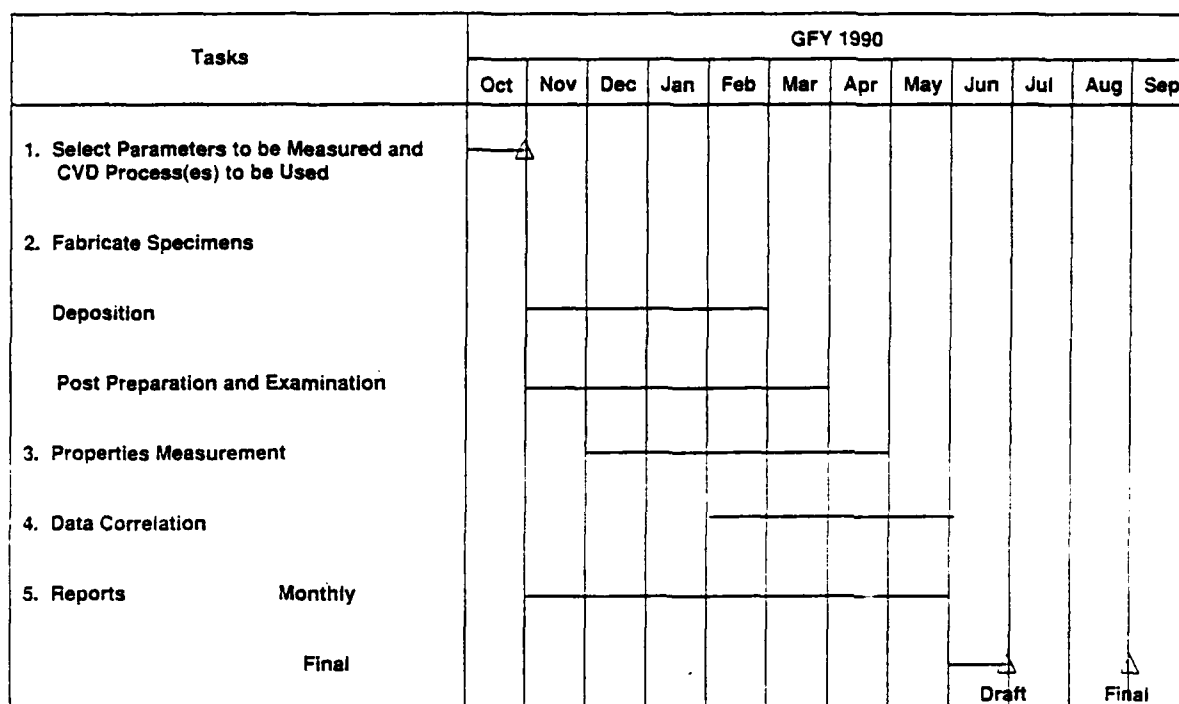


Figure 70. Properties determination for CVD diamond.

TABLE 45. Properties Determination Plan

Parameter	Deposition Process	Process Conditions	No. of Specimens	Test Conditions
1. Chemical Reactivity	DC Discharge	1A 1B 1C	12 12 24	Candidate TPA propellant(s)
2. Mechanical Adherence	DC Discharge	2A 2B 2C	12 12 12	Candidate environment
3. Compression Strength	DC Discharge	3A 3B	6 6	
4. Tensile Strength	DC Discharge	4A 4B 4C	12 12 24	
5. Young's Modulus	DC Discharge	5A 5B	6 6	
6. Friction Coefficient	DC Discharge	6A 6B 6C	12 12 24	Candidate propellants & environment
7. Hardness	DC Discharge	7A 7B	6 6	
8. Wear Rate	DC Discharge	8A 8B	6 6	Candidate propellants
9. Diffusion Coefficient	DC Discharge	9A 9B 9C	6 6 12	Candidate propellants
10. Thermal Expansion Coefficient	DC Discharge	10A 10B	6 6	
11. Thermal Conductivity	DC Discharge	11A 11B 11C	12 12 24	
12. Contact Stress	DC Discharge	12A 12B 12C	6 6 12	

tests in propellant environment, or tests requiring facilities not already set up and checked out.

A significant fraction of the resources would permit assurance that well-controlled synthesis techniques are used for specimen production and that sufficient specimens would be tested to provide statistical confidence in the data.

Procedures for a representative set of properties which meet the above criteria are described here.

6.2.1.1 Tensile Strength Measurements--The specimen configuration to be utilized for tensile evaluation is shown in Figure 71. The diamond film will be deposited on 0.050 in. Grade 4 unalloyed titanium. To prevent having to machine the coating, the titanium specimen will be machined into the final configuration, then the coating applied. This specimen configuration allows three specimens to fit in the area covered by a 4-in.-dia disk.

Pin holes will be drilled in the specimens prior to coating, and pins used to transfer load from the pullrods to the specimens. The deformation over the gage length will be measured with a pair of clip-on extensometers, one on each edge of the specimen. A schematic of the clip-on extensometer setup is shown in Figure 72.

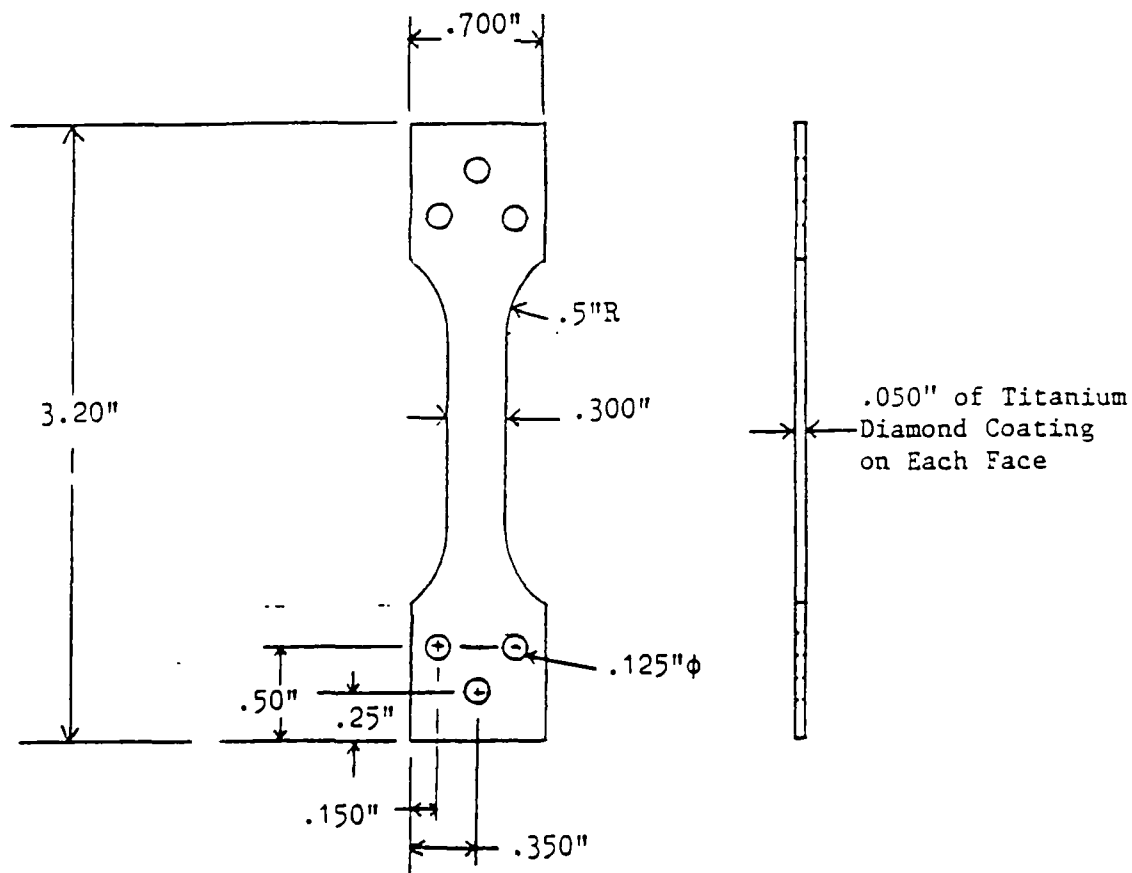


Figure 71. Tensile specimen configuration.

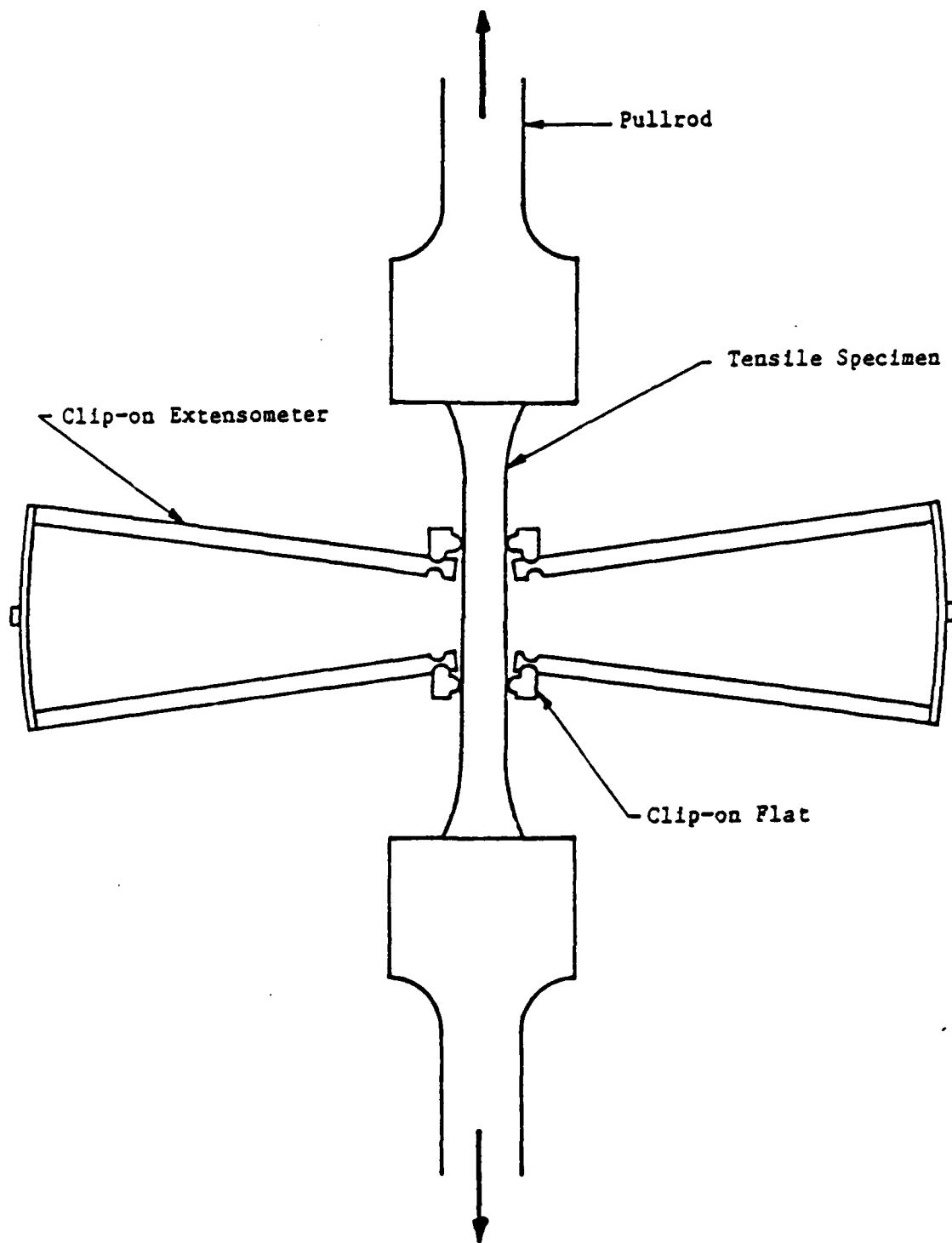


Figure 72. Schematic of clip-on extensometer set-ups for measuring tensile strain.

Figure 73 shows a portion of a typical stress-strain response for titanium and the predicted stress-strain response for a 0.050-in.-thick titanium specimen with a 0.005-in.-thick diamond coating on each face. The coating was assumed to have a modulus of 150 Msi and a strength of 250 ksi.

6.2.1.2 Compressive Strength Measurements--The specimen configuration to be utilized for the compressive evaluations is shown in Figure 74. Once again, the length of the specimen will be 3.2 in. so that three specimens can be coated at one time. The specimens will be laterally supported on both faces along the entire specimen length, except for an optimal unsupported region at the center of the specimen's length. The specimens will be loaded by anvils of nominally the same thickness as the specimen.

6.2.1.3 Contact Stress Measurement--Since the diamond film is to be utilized for coating bearings and races, the ultimate contact stress of the coating should be known. A schematic of a proposed test apparatus is shown in Figure 75. The test consists of loading a coated plate with a steel ball and then observing the coating for Hertzian cracks.

This is a procedure developed for study of thin, hard films for bearing applications. It determines, with a single procedure, the maximum allowable bearing contact load which is dependent on the combined physical properties of the film and substrates (such as tensile strength and modulus of elasticity) and the adequacy of the film bond.

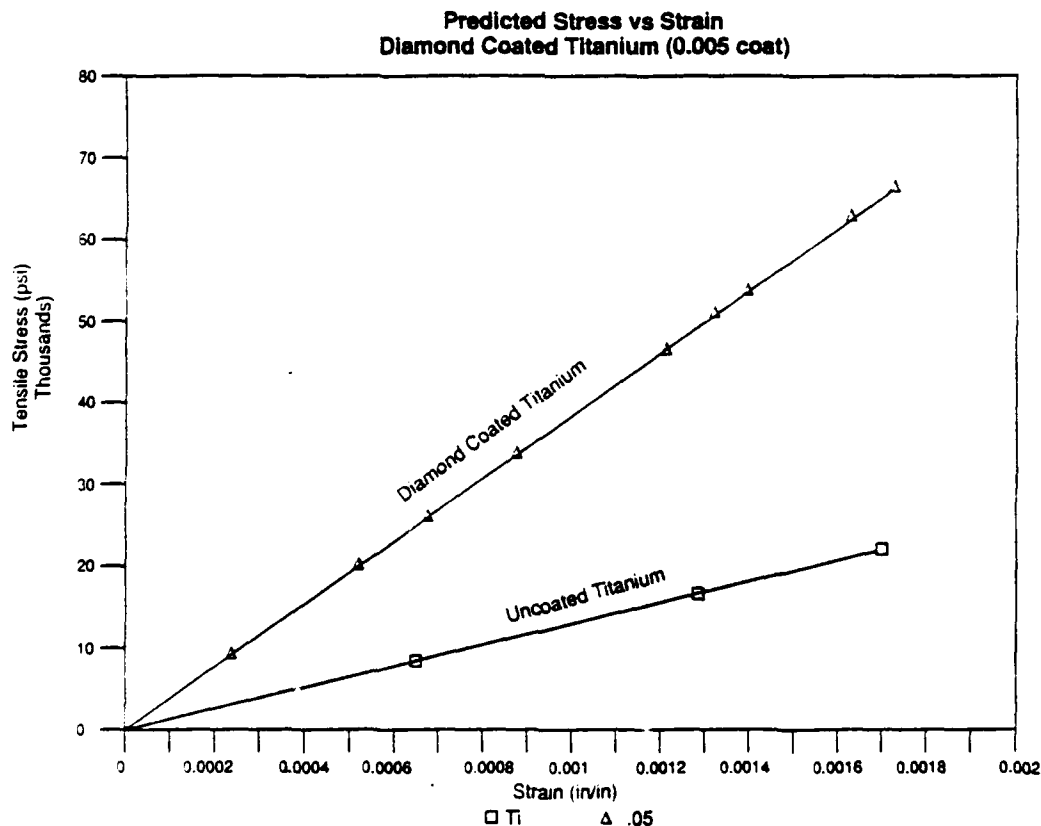


Figure 73. Predicted tensile stress-strain responses for uncoated titanium and diamond coated (0.005" coating) 0.05" thick titanium.

GROUP A.1.1.3

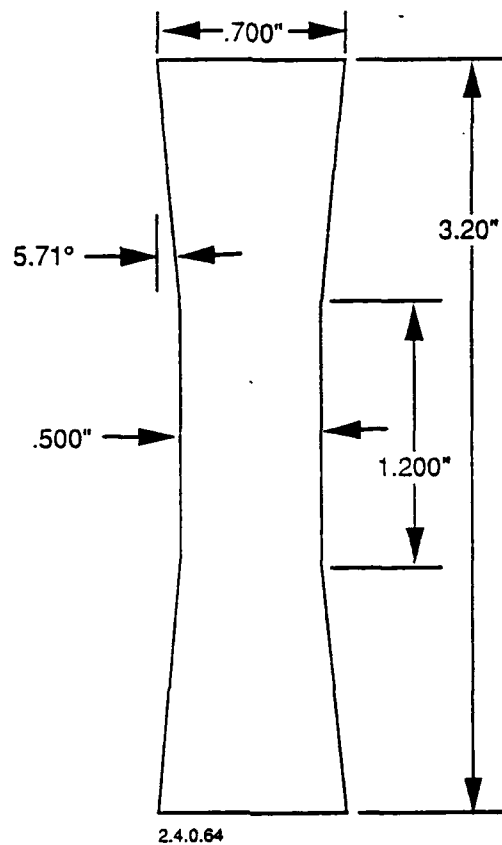


Figure 74. Compressive specimen configuration.

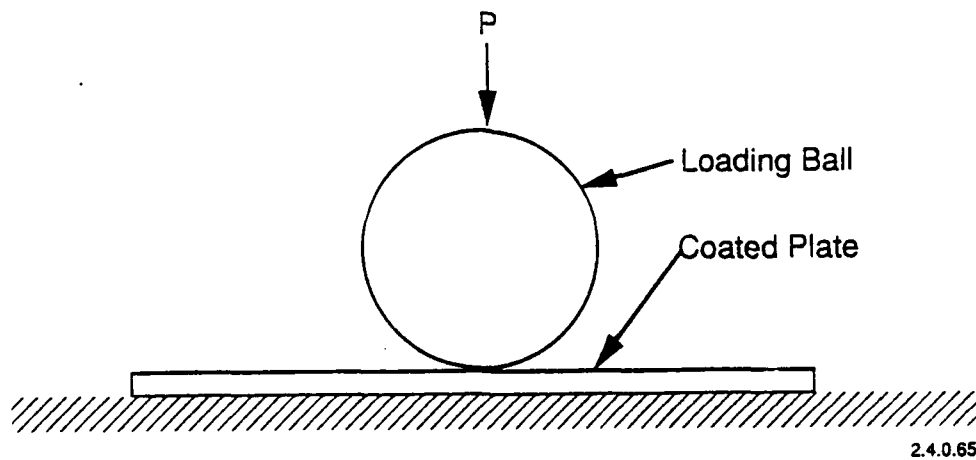


Figure 75. Contact stress schematic.

The plate will be machined from the same material as the bearing race will be manufactured from so as to provide support similar to that in actual application. Five load levels will be chosen. The load level at which cracking is first observed with the unaided eye or at low magnification will be recorded. Also, the specimen from the load level immediately prior to this will be observed using SEM techniques in an attempt to detect microcracking. In addition to this, knowing the maximum applied load and the material properties of the loading ball and the coating, the maximum obtained normal and shear stresses can be calculated for the coating using elastic contact stress equations.

6.2.1.4 Thermal Expansion Measurement--The thermal expansion specimen configuration to be utilized for these evaluations is shown in Figure 76. For these specimens, a coating 0.020 to 0.030 in. will be applied to silicon. The silicon will then be etched away, leaving a specimen consisting of the diamond coating only. The free-standing diamond specimen is then mounted between reference surfaces in a controlled-temperature oven. The temperature is set over the range of ambient to 800 C and the expansion of the diamond measured relative to NBS calibrated quartz dilatometer tubes.

6.2.2 Program Plan for Bearing Technology Demonstration

A program plan has been developed to assess the application of diamond films for bearings, seals, and other tribological uses. There are three main tasks to this evaluation. The first task consists of a fabrication demonstration to establish feasibility for depositing diamond films on specific substrates and certain configurations. The second task consists of properties evaluation which are key for rocket engine applications. The third and final task of this effort will select a component, e.g., a bearing or a face seal, and then design, fabricate, and test it in a rocket engine environment to demonstrate life and performance improvement.

A schedule for this activity has been prepared and is shown in Figure 77. A task-by-task description is presented. The resources required are estimated to be eight person-years over the three-year program.

Task 1.0 - Fabrication Demonstration--This task will address two key issues for diamond film fabrication. The first consists of substrate material. Diamond can be deposited on molybdenum and molybdenum alloys such as TZM; however, other candidate substrate materials must be evaluated. The first part of this task will select a minimum of three alloys, such as those listed above in the technical discussion, which are typically used in wear or rubbing applications. These materials will be procured and used for deposition studies. Parametric deposition studies will be conducted to develop an optimum coating for each material. Thicknesses ranging from 12.7 to 254 micron (0.0005 to 0.0100 in.) will be deposited for evaluation. The evaluation will include visual and SEM examination for surface defects, Raman spectroscopy, and X-ray diffraction for crystallographic phase identification. Metallographic sections will be prepared to check for microstructure and any other anomalous features such as porosity. Special emphasis

DIAMOND FILM BEARING SURFACE STUDY SCHEDULE

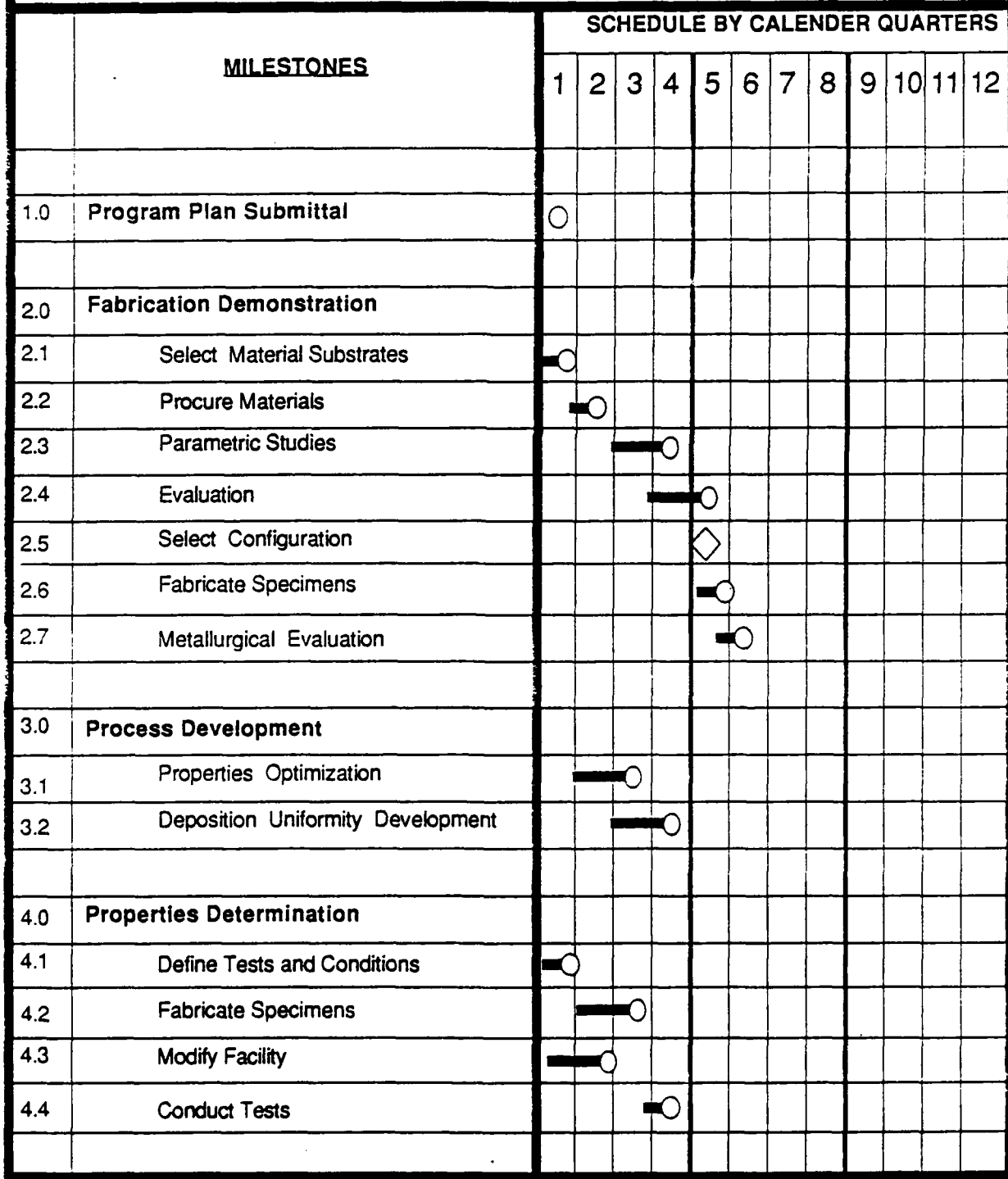


Figure 77. Diamond film bearing surface study schedule, page 1 of 2.

DIAMOND FILM BEARING SURFACE STUDY

SCHEDULE

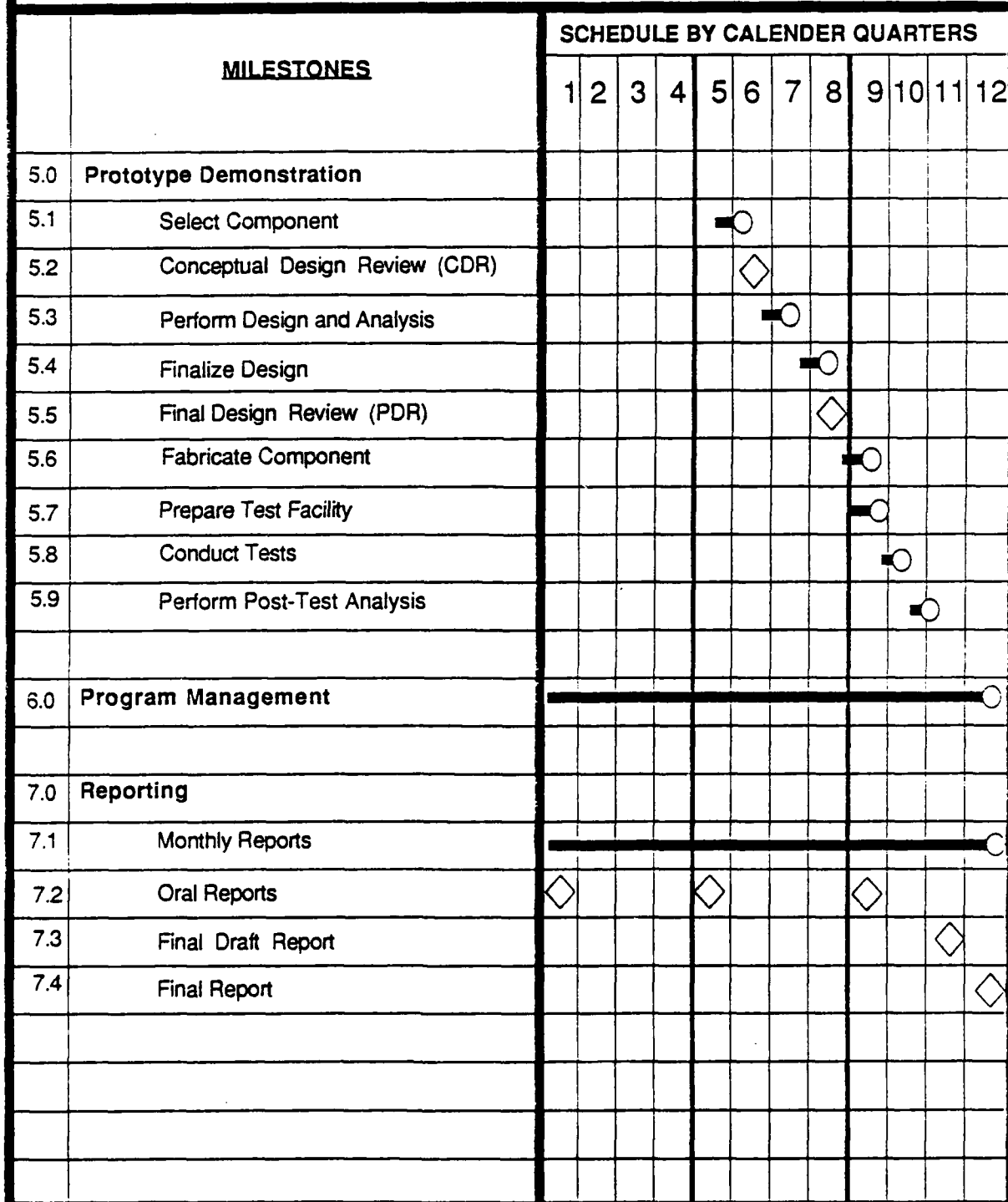


Figure 77. Diamond film bearing surface study schedule. page 2 of 2.

will be devoted to examining the bond interface. Other specimens will be thermally cycled up to 1000 C and examined to check for bond adherence.

The second part of this task will demonstrate coating configuration. Three candidate applications, such as bearing rolling elements, races, and seals, will be selected. Specimens will be produced from materials which were demonstrated to be viable substrates in the first part of this task. These specimens will have diamond films of the appropriate thickness deposited on them and then evaluated. The evaluation will be similar to that done above, except special emphasis will be placed on thickness uniformity.

Task 2.0 - Properties Determination--A series of tests will be conducted to determine key properties of diamond. These tests deal primarily with measuring the coefficient of friction of diamond films in appropriate propellant operating environments. These tests will include environments such as oxygen or hydrogen. The tests will be defined on the program, but they will probably be either pin-on-plate or traction-rig tests. Appropriate substrates will also be selected, i.e., for tests conducted in hydrogen, titanium alloys would be a proper substrate.

These data will be assembled and used to generate designs for Task 3.0.

Task 3.0 - Prototype Demonstration--This final task will demonstrate performance and life improvement attainable with diamond films on a selected specimen. Based on the work conducted in Task 1.0, a candidate subcomponent, such as a face seal, will be selected for design, fabrication, and test. The component selection and the AFAL approval will be influenced by available test facilities. The tests will be performed to simulate operating loads and environments. Once the component has been selected, a mechanical design will be prepared using the data developed in Task 2.0. Analytical models will be prepared and evaluated to determine life and performance improvements. These data will be used to finalize the design.

The component will then be fabricated and tested to verify the model's predictions.

Task 4.0 - Management and Reporting--A separate task will be established to handle monthly and final reports and to insure proper direction and guidance on the program.

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APPENDIX A

DIAMOND FILM SURVEY RESPONSES

APPENDIX A

INTRODUCTION

The following pages contain data transcribed from the survey responses with information which would identify the group removed. To maximize the extent of information transfer, a separate set of data is provided which identifies the personnel and papers as provided in the survey questionnaires.

TABLE A-1. Survey Response Data Tabulation (1 of 24)

2. Period of activity	Since December, 1984
3. Areas being investigated	a. Deposition by Ion Beam Enhanced Deposition techniques. (IBED) b. Energetics of diamond film formation from pure carbon. c. Growth of films on metals (ferrous and non-ferrous), ceramics, plastics, and glass. d. Optimization of film-substrate adhesion. e. Characterization of film morphology, crystallinity, chemical composition, and chemical binding. f. Boping of films to optimize mechanical, electrical, and optical properties. g. Measurement of mechanical, electrical, and optical properties. h. Applications to mechanical, electrical, and optical components.
4. Properties measured	a. Percentage of sp³ hybrid orbital bondings (> 93%), via carbon KLL Auger electron spectroscopy. b. Coefficient of friction against dry, unlubricated tool steel in air: 0.08. c. Hardness: 4500 - 5000 DPHM at Natural diamond 6000 DPHM. d. Electrical resistivity: 10E(08) - 10E(10) ohm-cm e. Optical transparency (on transparent substrates): excellent.
5. Deposition parameters	a. Pure carbon is ion beam sputter deposited and simultaneously illuminated with a variable, medium energy Argon ion beam. b. Vacuum pressure: 10E(-04) Torr. c. Temperatures: 150 degrees Fahrenheit.
6. Precursors	<i>Precursor is pure Carbon, generated by ion beam sputtering of a pure graphite sputtering target.</i>
7. Production techniques for atomic hydrogen	a. Investigating dopant additions such as nitrogen to optimize mechanical properties. b. Atomic hydrogen is not required to either nucleate or preferentially getter graphite.
8. Deposition rates	a. ION BEAM ENHANCED DEPOSITION (IBED) TECHNIQUES. b. Current deposition rate: 3 Angstroms per minute over an eight (8) inch diameter target area. c. Deposition rate in 2 years: 50 Angstroms per minute over an eighteen (18) inch diameter target area. (System now under construction) d. Deposition rate in 5 years: 500 Angstroms per minute. e. Deposition rate in 10 years: 5000 Angstroms per minute.
9. Characterization methods	a. Auger Electron Spectroscopy. b. Laser Raman Spectroscopy c. Scanning Electron Microscopy.
10. Forms other than films	Not currently
11. Processes other than low pressure CVD or PVD	Ion Beam Enhanced Deposition is our primary focus.
12. Minimum deposition temperature	Approximately 100 Fahrenheit.
13. Applications/stage	a. Mechanical components: wide variety of tools and wear parts. b. Electrical components: computer disks, magnetic tape recording heads. c. Optical components: plastic and glass lenses and windows, windows for optical and infrared sensors. d. Medical components: inert surfaces for implantables, wear and lubricating surfaces for orthopedic devices. at concept stage? All investigations are at the development stage.
15. Comments on status/areas requiring work/applications	Applications for diamond films will develop slowly over the next 2 to 5 years. More knowledge must be generated on the exact morphology, crystalline structure, and chemical composition of the films to enable proper choice of film type for specific applications. This is particularly true in semiconductor device applications. More knowledge must also be generated about how the films grow and the relationship of film growth mechanisms with the chemistry and metallurgy of substrate surfaces they are to be deposited on. A number of refinements related to deposition techniques and technologies must be made before production is

TABLE A-1. Survey Response Data Tabulation (2 of 24)

technically and economically feasible. We believe that these refinements are possible. Specific, separate applications will develop for the films as deposited by PECVD and IBCD techniques due to the very different process pressure and temperature requirements of each.

TABLE A-1. Survey Response Data Tabulation (3 of 24)

2. Period of activity	7-84
3. Areas being investigated	Deposition technology--high rates, large area, low temperature
4. Properties measured	adhesion, thermal conductivity, electronic properties
5. Deposition parameters	DC: 25 Torr, 725 C 350 v, 0.51 CM4 Microwave: 50 Torr, 850C, 1 km, 0.21 to 1.0 1 CM4
6. Precursors	Methane; exploratory work with CO
7. Production techniques for atomic hydrogen	Electrical ionization
8. Deposition rates	Presents: DC 0.01 to 1.0 micron/hr; microwave 0.1 to 5 micron/hr
9. Characterization methods	Futures: two years "21 above, five years "41 above, and "50 micron/hr using arc jets; ten years no improvement on DC and microwave, "500 micron/hr using arc jet
10. Forces other than files	Raman spectroscopy, IR thermal conductivity measurements, SEM, optical microscope, He leak detector, alpha-step surface profiler
11. Processes other than low pressure CVD or PVD	Yes. Have coated Si3N4 fibers and are researching the production of diamond particles and fibers
12. Minimum deposition temperature	370C on Au-Si alloy
13. Applications/stage	I-ray spectrometer window (production), heat sinks for electronics (in development)
15. Comments on status/areas requiring work/applications	Diamond film technology faces the following limiting factors today: deposition area is too small for many applications (e.g. canopy coating); deposition rates are too low for good economy in some applications (e.g. thick microwave windows); adhesion is poor on some very important substrate materials (e.g. InS, ZnSe, steel, and Ni-based superalloys); surface morphology limits some optical applications (e.g. scatter due to surface roughness and internal defects); absence of good n-type semiconducting diamond limits electronic applications. Earliest applications are likely to be laboratory sensor windows (eg. I-ray spectrometer window), heat sinks

TABLE A-1. Survey Response Data Tabulation (4 of 24)

2. Period of activity	Two years
3. Areas being investigated	Deposition methods, primarily; secondary interest in properties and chemistry
4. Properties measured	Crystal structure, hardness, chemical resistance
5. Deposition parameters	
6. Precursors	Hydrocarbons; O and/or N containing compounds, etc.
7. Production techniques for atomic hydrogen	Hot filament and a type of plasma
8. Deposition rates	Now several to tens of microns/hr; several hundreds micron/hr in future
9. Characterization methods	Thin film X-ray diffraction; Raman spectroscopy
10. Areas other than films	Particulate single crystals and polycrystalline
11. Processes other than low pressure CVD or PVD	Combustion
12. Minimum deposition temperature	500 C
13. Application/stage	Hard coatings/conceptual
15. Comments on status/areas requiring work/applications	Expecting very high potential applications in the future

TABLE A-1. Survey Response Data Tabulation (5 of 24)

2. Period of activity	Six to seven years
3. Areas being investigated	Deposition
4. Properties measured	
5. Deposition parameters	
6. Precursors	
7. Production techniques for atomic hydrogen	RF plasma, microwave plasma, and hot filament
8. Deposition rates	Approx. 1 microm/hr
9. Characterization methods	Cutting test
10. Forms other than films	No
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	Approx. 800 C
13. Application/stage	Coating on super hardened alloy
15. Comments on status/areas requiring work/applications	

TABLE A-1. Survey Response Data Tabulation (6 of 24)

2. Period of activity	Since 10-87
3. Areas being investigated	Chemistry, Deposition Technology, Properties of Materials, Device Fabrication.
4. Properties measured	Raman, P.L., IRB, e channeling, AES, SEM, EPR, Results varied.
5. Deposition parameters	Varied
6. Precursors	Various
7. Production techniques for atomic hydrogen	Hot filament, microwave, combustion flame.
8. Deposition rates	.1 to 200 microns/hour; hard to guess future capability
9. Characterization methods	Raman, IPS, AES, SEM, IRB, EPR, P.L., EPR, IR, VIS, UV, ELS.
10. Foras other than films	YES
11. Processes other than low pressure CVD or PVD	YES
12. Minimum deposition temperature	600C
13. Application/stage	Varied, at concept stage? yes, at development stage? yes
14. Reports	
15. Comments on status/areas requiring work/applications	

TABLE A-1. Survey Response Data Tabulation (7 of 24)

2. Period of activity	Two years
3. Areas being investigated	Thermal properties, mechanical strength, porosity, electrical conductivity, Raman spectra, I-ray spectra, impurity concentration, microwave transmission from 100 GHz to 100 THz, crystal structure, impact of deposition parameters on crystal size structure, adhesion of diamond film to substrates, improvements in using buffer layer.
4. Properties measured	Electrical conductivity, microwave transmission, thermal conductivity, thermal cycling capability
5. Deposition parameters	1% methane, 99% hydrogen-900 C-1000 C using 1 kw microwave power at 200 watts per square centimeter.
6. Precursors	Buff the surface with diamond powder 0.25 - 1 micron. The wafer is etched in atomic hydrogen before deposition.
7. Production techniques for atomic hydrogen	Microwave discharge only.
8. Deposition rates	0.3 - 1 micron per hour using microwave power. Predictions 0.3 - 5 microns per hour.
9. Characterization methods	Principally, Raman scattering, optical micrographs and SEM. Secondly, electric conductivity, thermal conductivity (pulse laser technology), microwave transmission using Fourier transform spectroscopy, mechanical strength using window deflection for 0 - 1 atmospheres.
10. Forms other than films	No
11. Processes other than low pressure CVD or PVD	Not at present
12. Minimum deposition temperature	800 C; up effort has been made to lower temperature.
13. Application/stage	A) Microwave windows (development stage) B) Coatings on ceramic tools (development stage) C) Coatings for biomedical parts (development stage) D) Diamond heat sinks (concept stage)
15. Comments on status/areas requiring work/applications	We have made significant progress in a short time. With a technology that is easy to start, there is a great future. We envision window and cutting tool applications being near-term. Additional work: Increase nucleation density by a factor of 10 or higher. It is important to improve uniformity over a large area and to pursue catalysis for faster growth rate.

TABLE A-1. Survey Response Data Tabulation (8 of 24)

2. Period of activity	Laboratory established six months ago.
3. Areas being investigated	Nucleation and growth, heteroepitaxial films, thermal properties, electrical properties.
4. Properties measured	Thermal properties by thermal wave method
	Result: rapid, contact less measurement of thermal conductivity in situ
	Raman spectrum verify the presence of diamond
5. Deposition parameters	Microwave PECVD, 100 Torr, 1550 SCCM H ₂ , 10 SCCM CH ₄
6. Precursors	CH ₄ , Water
7. Production techniques for atomic hydrogen	Microwave
8. Deposition rates	0.5 microns/hr.
9. Characterization methods	Raman thermal wave, conductivity
10. Forms other than films	Not at this time.
11. Processes other than low pressure CVD or PVD	Yes
12. Minimum deposition temperatures	Currently 800C
13. Application/stage	Proprietary information
15. Comments on status/areas requiring work/applications	Diamond film technology is at a very early developmental stage. a. area that needs to be developed is our understanding of nucleation and growth as a function of precursor gases. I believe the nearest term applications are for wear coatings and heat sinks.
17. Other researchers who should be contacted	R. Herrier, Penn State, N. Reis, LLNL, A. Galdano, NIST, T. Perry, GM, J. Glass, NCSU.

TABLE A-1. Survey Response Data Tabulation (9 of 24)

2. Period of activity	Two years.
3. Areas being investigated	Electrical and thermal properties.
4. Properties measured	Thermal conductivity, 1000 W/MK Electrical resist
5. Deposition parameters	
6. Precursors	CH ₄ /H ₂
7. Production techniques for stoichiometric hydrogen	Microwave discharge
8. Deposition rates	1 nm/hr
9. Characterization methods	SEM, Raman, X-Ray, I-V Curves
10. Forms other than films	Films
11. Processes other than low pressure CVD or PVD	Not at this time.
12. Minimum deposition temperature	800C
13. Application/stage	Heat sinks at concept stage.
15. Comments on status/areas requiring work/applications	
17. Other researchers who should be contacted	

TABLE A-1. Survey Response Data Tabulation (10 of 24)

2. Period of activity	Four Months
3. Areas being investigated	Deposition, properties, chemistry, gas phase species, Surface active species, Optical properties, Thermal properties, Characterization.
4. Properties measured	Optical - good LMIR transmission
5. Deposition parameters	I-ray - Bismuth
6. Precursors	Heavy seeding
7. Production techniques for atomic hydrogen	Methane and Hydrogen
8. Deposition rates	Microwave Plasma and Astec System.
9. Characterization methods	5 microns/hr
10. Forces other than films	Optical, Thermal, Mechanical, I-ray, Auger, SEM, Optical Microscopy, Chemical.
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	Yes
13. Application/stage	800C LMIR at concept stage? YES at development stage? YES or at production stage? NO Needs more work.
15. Comments on status/areas requiring work/applications	

TABLE A-1. Survey Response Data Tabulation (11 of 24)

2. Period of activity	Four years
3. Areas being investigated	Deposition techniques; characterization using surface analysis techniques
4. Properties measured	Data not available until April '89
5. Deposition parameters	
6. Precursors	H ₂ and CH ₄
7. Production techniques for atomic hydrogen	Microwave
8. Deposition rates	0.8 micron/hour
9. Characterization methods	ESCA, AES, Raman, SEM, SAM
10. Foras other than films	No
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	500 C (on silicon)
13. Application/stage	Electronics
15. Comments on status/areas requiring work/applications	Semiconductors

TABLE A-1. Survey Response Data Tabulation (12 of 24)

2. Period of activity	Five years
3. Areas being investigated	Source gas, properties, semiconductors
4. Properties measured	Hardness, electroconductivity, transparency, adhesiveness,
5. Deposition parameters	
6. Precursors	Carbon monoxide/hydrogen mix
7. Production techniques for atomic hydrogen	Microwave
8. Deposition rates	2 to 3 micrometers/hour now; expect 20 to 30 in 5 years
9. Characterization methods	Raman spectroscopy, X-ray diffraction, SEM, TEM
10. Forms other than films	Powders and single crystals
11. Processes other than low pressure CVD or PVD	None
12. Minimum deposition temperature	400 C now; expect 350 to 400 C in near future.
13. Application/stage	Cutting tools/production; Semiconductors/development; three dimensional LSI/conceptual
15. Comments on status/areas requiring work/applications	
20. General discussion	Carbon monoxide is one of the best sources. Diamond cutting tool market is not large; semiconductor market will be large.

TABLE A-1. Survey Response Data Tabulation (13 of 24)

2. Period of activity	18 months
3. Areas being investigated	Deposition; nucleation mechanisms; growth rate, parametric investigations; adhesion; substrate effects. New methods: Developed a hollow-cathode reactor for diatomic deposition
4. Properties measured	Many data have been published
5. Deposition parameters	Hot filament or hollow cathode systems (tables in enclosed publications)
6. Precursors	Methane/H ₂ . Others are under study but info is proprietary
7. Production techniques for atomic hydrogen	Thermal and plasma dissociation
8. Deposition rates	3-6 microns/hour now, future factor of 2x per year for the next 5 years
9. Characterization methods	I-ray, Raman, RHEED, LEED, SEM
10. Forces other than films	Particles
11. Processes other than low pressure CVD or PVD	no
12. Minimum deposition temperature	600-650C
13. Application/stage	Heat sinks, free-standing films, single-crystals (electronics, optics). At concept stage.
15. Comments on status/areas requiring work/applications	Work needed: 1, detailed mechanisms of nucleation, 2) integrated chemistry/physics approach to growth rates, 3) absolute chemical yields, 4) process cont. Application Assessment: Few real applications in the commercial sector until deposition temperature can be reduced

TABLE A-1. Survey Response Data Tabulation (14 of 24)

2. Period of activity	Three years
3. Areas being investigated	Deposition, properties
4. Properties measured	
5. Deposition parameters	
6. Precursors	
7. Production techniques for atomic hydrogen	Microwave, tungsten filament, Electron cyclotron resonance
8. Deposition rates	Microwave 3 micron/hr on 20x20mm area Tungsten filament 1 micron/hr on 50x100mm
9. Characterization methods	SEM, I-ray, Raman, Cathodoluminescence
10. Forces other than films	Diamond particles
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	750 C
13. Application/stage	Tools, electronic parts/development
15. Comments on status/areas requiring work/applications	

TABLE A-1. Survey Response Data Tabulation (15 of 24)

2. Period of activity	2 years
3. Areas being investigated	Optimizing deposition parameters, determining the structure of the films characterizing the film properties, and investigating applications.
4. Properties measured	The films were characterized for their structural composition using grazing incidence Laue x-ray diffraction. The films generated from the hot-filament CVD system were characterized as diamond by this method. Scanning electron microscopy was performed on the films, and they exhibited a smooth surface morphology which is atypical of the technique. The smoothness is attributed to the low pressure regime. The deposition pressure of 1.5×10^{-4} torr is six orders of magnitude lower than what is typically reported for hot-filament CVD.
5. Deposition parameters	Gas concentrations: 1.05 CH ₄ in H ₂ , Flow Rate: 50 SCCM Substrate temperatures: 800 C, Filament temperature 2000 C. Deposition rate: 20 Å/min, Pressure: 1.5×10^{-4} torr
6. Precursors	1-3 I ethane in hydrogen gas.
7. Production techniques for atomic hydrogen	A filament of 20 turns of 0.15mm diameter tungsten wire is used. We plan to investigate the use of a hollow cathode to produce the atomic hydrogen.
8. Deposition rates	For typical deposition conditions, the deposition rate is 20 Å/minute. Unable to estimate future deposition rates at this time.

TABLE A-1. Survey Response Data Tabulation (16 of 24)

2. Period of activity	Five years
3. Areas being investigated	Fabrication of diamond coated tools
4. Properties measured	Thermal conductivity: 1,900 W/m ² ; Vickers hardness: >10,000 kg/mm ² ; Specific gravity: 3.5; Relative dielectric constant: 4-0.5; Resistivity: >10 E14 ohm-cm
5. Deposition parameters	EACVD: 40 torr; 50 sccm; 0.5 to 2 % CH ₄ ; 10 mW/cm ² ; 1 to 20 hours; 1200 °C; on W, cemented carbide; 700 to 900 °C
6. Precursors	DC Plasma CVD: 200 torr; 50 to 200 sccm; 0.5 to 5 % CH ₄ ; 1000 mW/cm ² ; 1 cm ² on cemented carbide, Si; 800 to 1000 °C
7. Production techniques for atomic hydrogen	CH ₄ + H ₂
8. Deposition rates	Hot filament; DC discharge
9. Characterization methods	EACVD 5 micron/hour; DC plasma 20 micron/hr.
10. Forces other than files	Expect to get 500micron/hr in the future
11. Processes other than low pressure CVD or PVD	Raman, RHEED, X-ray, SEM, hardness
12. Minimum deposition temperature	High pressure sintered diamond compact
13. Application/stage	None
15. Comments on status/areas requiring work/applications	650 °C Turning tools, drilling tools, machine parts. In development and production. For practical applications must enhance the adhesion between the base material and CVD diamond

TABLE A-1. Survey Response Data Tabulation (17 of 24)

2. Period of activity	1 1/2 years
3. Areas being investigated	Deposition parameters and properties.
4. Properties measured	Hardness - diamond
	Wear resistance - favorable
	Similar to literature reports
5. Deposition parameters	CM
6. Precursors	Microwave, others
7. Production techniques for atomic hydrogen	2 yrs, 1 micron/hour - 500 micron/hour
8. Deposition rates	3 yrs, 1 micron/hour - 1000 micron/hour
9. Characterization methods	I-ray, Ra
10. Forms other than films	Films
11. Processes other than low pressure CVD or PVD	Yes
12. Minimum deposition temperature	950C
13. Application/stage	Wear applications at development stage.
15. Comments on status/areas requiring work/applications	Early applications development stage. Need study of basic mechanisms and scale-up.
17. Other researchers who should be contacted	Jim Butler, MRL Ray Decker, Mavesat, Plymouth, Mich.

TABLE A-1. Survey Response Data Tabulation (18 of 24)

2. Period of activity	For over 25 years.
3. Areas being investigated	Deposition of both CVD diamond and DLC. Chemistry of nucleation process. Properties of CVD diamond. Properties of diamond-I Theory of diamond surface and heteroepitaxy. Engineering design of deposition chamber.
4. Properties measured	Hardness, density, fraction of DLC present, mechanical properties, adhesion, morphology, elemental analysis.
5. Deposition parameters	Varies widely depending on substrate and desired properties.
6. Precursors	We consider this proprietary information.
7. Production techniques for atomic hydrogen	Hot filament, DC glow discharge, hot filament plus electron bombardment, RF discharge (for
8. Deposition rates	Varies widely depending on Application. Impossible to predict.
9. Characterization methods	Raman, EELS, elemental analysis, both H and heavy element, density, X-Ray, electron microscopy.
10. Forms other than films	Yes
11. Processes other than low pressure CVD or PVD	Yes, we are actively exploring other methods.
12. Minimum deposition temperature	The "true" surface temperature is very difficult to know accurately.
13. Application/stage	Substrates for electronic devices, a/s/electronic packaging, computer disk coatings, vapor barriers, corrosion resistant coatings.
15. Comments on status/areas requiring work/applications	Still a very immature field, but with many opportunities.

TABLE A-1. Survey Response Data Tabulation (19 of 24)

2. Period of activity	3 years
3. Areas being investigated	RF plasmas/microwave plasmas/aethane/ diacord and DLC filia (alpha-C, C ₁₈ H, 1-C)
4. Properties measured	Hardness--scratch resistant; chemical inertness-- resists HF, HNO ₃ , H ₂ SO ₄ , H ₃ PO ₄ , HCl, solvents; optically transparent; x-ray totally amorphous; $\rho \sim 2.3, \rho \sim 2.8$ sp ² -3110E7 V/cm, rho ² -10E15 ohm-cm; SIMS-1-101 H; SEM-smooth surface
5. Deposition parameters	see abstract
6. Precursors	no data
7. Production techniques for atomic hydrogen	no data
8. Deposition rates	0.1-1 micron/hr (Japanese are doing >1 micron/min); 7 years 1 micron/min; 10 years 10 micron/min
9. Characterization methods	SIMS, Raman, ESCA, SEM, TEM, X-RAY, SAM, capacitor structures
10. Forces other than filia	no
11. Processes other than low pressure CVD or PVD	no
12. Minimum deposition temperature	Do just DLC
13. Application/stage	Capacitor, dielectric filia/at development stage
15. Comments on status/areas requiring work/applications	No true heteroepitax pure sp ³ filia (>100M) internal stress a major issue/cold substrate; H ₂ as etchant, high activation state of C but low k.o. essential

TABLE A-1. Survey Response Data Tabulation (20 of 24)

2. Period of activity	Two years
3. Areas being investigated	Crystal growth
4. Properties measured	Interplanar spacing measured by x-ray in good agreement with values reported in ASTM 6-675j only one peak at 1333 cm^{-1} from Raman measurements
5. Deposition parameters	Pressure: 40 torr; methane concentration 1 to 10 %; hydrogen flow, 50 to 200 cc/min; power 250 to 500 W
6. Precursors	Methane
7. Production techniques for atomic hydrogen	Microwave
8. Deposition rates	Typical 0.5 to 3.0 $\mu\text{m/hr}$. Anticipate 100 $\mu\text{m/hr}$
9. Characterization methods	x-ray diffraction and Raman spectrum
10. Foras other than films	No
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	About 800 C
13. Application/stage	Semiconductors/conceptual with some development
15. Comments on status/areas requiring work/applications	Growth mechanism; technology of commercial production; impurity doping for electronic applications

TABLE A-1. Survey Response Data Tabulation (21 of 24)

2. Period of activity	Five years
3. Areas being investigated	Growth methods for diamond thin films by CVD
4. Properties measured	Have measured hardness, density, surface roughness, adhesion, thermal conductivity, electrical resistivity, dielectric constant, dielectric strength, and oxidation stability.
5. Deposition parameters	Electron assisted CVD and DC plasma CVD
6. Precursors	EMCVD 2 to 5 micron/hour; DC plasma CVD 10 to 20 micron/hour. In near future expect 3 to 4 times increase in growth rate.
7. Production techniques for atomic hydrogen	X-ray and electron diffraction, transmission electron microscopy, SEM, Raman spectroscopy, IR spectroscopy, electron energy loss spectroscopy, Secondary ion spectroscopy, laser microprobe mass analysis
8. Deposition rates	Also investigating particles and plates
9. Characterization methods	No comment
10. Focus other than films	700 to 800 C
11. Processes other than low pressure CVD or PVD	Various functional uses in electronics field. No comment on stage of development.
12. Minimum deposition temperature	In 21st century Market. for new diamond materials and devices will be extremely extended by promotion of such technologies as semiconductor by the electronics industry
13. Application/stage	Work is required on substantial growth of diamond thin films on foreign substrates, growth of large single crystal diamond, low temperature synthesis, high growth rate synthesis, clarification of the growth mechanism at low pressure, and adhesion to substrate.
14. Comments on status/areas requiring work/applications	Assessment of applications: Cutting tools/production; heat dispersion devices/conceptual and development; semiconductor devices/conceptual and development; Much research is required to realize industrial production of diamond grown from the vapor phase.

TABLE A-1. Survey Response Data Tabulation (22 of 24)

2. Period of activity	One year
3. Areas being investigated	1. Plasma assisted CVD processes. 2. Relationship between process parameters and film properties. 3. Polycrystalline, p-type diamond. 4. Monocrystalline diamond films. 5. Film deposition at low temperatures. Schottky diodes and MOSFETs have been fabricated on monocrystalline p-type diamond curves were obtained. Only measured properties are microstructure and Raman spectra. Resistivity measurements are not yet completed. Plasma enhanced CVD, 20-40 Torr, independently heated substrate, certain energy-assist techniques contemplated. Proprietary Plasma excitation. Other methods being investigated; cannot comment. We believe atomic hydrogen is not as important in film nucleation and growth as predicted in earlier thermodynamic and chemical kinetic models. There is a trade-off between rate and film properties. We are less interested in deposition rate and more interested in creating diamond films of desirable properties. Optical microscopy, scanning electron microscopy, Raman spectroscopy, 4-point probe. Yes. We have successfully synthesized diamond particles by homogeneous nucleation. A manuscript has been submitted to J.Appl.Phys. Yes. Approaches are company confidential at this time. Approximately 500 degrees C for diamond, 25 degrees C for DLC (optically transparent, colorless, Mohs = ~ 8). We have a BoE Press J SBR contract to create an edge-supported membrane of blue diamond. 2 cm in diameter, 1/16 inch thick. This work will be discussed at the Electrochemical Society Meeting, May 1989. Our IR & D programs are pursuing semiconducting diamond films. We have fabricated Schottky diodes, MOSFETs & MESFETs with assistance from Dr. H. Beis at Lincoln Labs. We are also pursuing development of diamond and DLC coatings. Are these at concept stage? sintered diamond powders at development stage? Yes; (semiconductor & optical devices)
4. Properties measured	
5. Deposition parameters	
6. Precursors	
7. Production techniques for atomic hydrogen	
8. Deposition rates	
9. Characterization methods	
10. Forms other than films	
11. Processes other than low pressure CVD or PVD	
12. Minimum deposition temperature	
13. Application/stage	
15. Comments on status/areas requiring work/applications	The U.S. stands a serious chance of being overwhelmed by the Japanese in the science and technology of low-pressure diamond. Japanese tool companies are poised to introduce novel diamond-coated tools in the U.S. market. Federal government support of low-pressure diamond is inadequate. The U.S. needs to immediately fund multi-million dollar R&D programs on: (1) basic science of diamond deposition, (2) study of adhesion/cohesion forces to diamond, (3) replacement of InS and InSe IR materials with diamond, and (4) characterization and passivation of grain boundaries in diamond films. Dr. Karl Spear, Penn State Dr. H. Beis, Lincoln Labs.
17. Other researchers who should be contacted	

TABLE A-1. Survey Response Data Tabulation (23 of 24)

2. Period of activity	Three years
3. Areas being investigated	Depositions application
4. Properties measured	Crystal Structure; Thermal conductivity; 800 m/s K; hardness; 10,000 Kg/mm ² ; Electrical resistivity; 10E4 to 10E5 ohm cm; phonon structure
5. Deposition parameters	
6. Precursors	
7. Production techniques for atomic hydrogen	DC discharge
8. Deposition rates	Now achieve 0.2 nm/hr and anticipate 1 nm/hr
9. Characterization methods	I-ray diffraction, Raman spectroscopy, Vicker's hardness, thermal conductivity
10. Forces other than films	No
11. Processes other than low pressure CVD or PVD	No
12. Minimum deposition temperature	800 C
13. Application/stage	Heat sink for laser diode packages; development; circuit boards; conceptual; Hard coatings; conceptual
15. Comments on status/areas requiring work/applications	Study of growth mechanism and nucleation mechanism Adhesion to substrate for hard coating Polishing and cutting technology

TABLE A-1. Survey Response Data Tabulation (24 of 24)

2. Period of activity	About ten years
3. Areas being investigated	All areas
4. Properties measured	Hardness (Vickers); 10,000; Dielectric constants; about 5.8; resistivity (degad); 10E12 ohm cm; optical transparency
5. Deposition parameters	Hydrocarbons e.g. methane
6. Precursors	Hot filament and microwave plasma CVD
7. Production techniques for atomic hydrogen	Expect to get 100 micron/hr in the future, depending on the quality of the diamond film
8. Deposition rates	Raman spectra; reflective electron diffraction, X-ray diffraction
9. Characterization methods	Thick film, etc.
10. Forms other than films	Yes
11. Processes other than low pressure CVD or PVD	About 700 C
12. Minimum deposition temperature	Diamond coated speaker diaphragm/commercialized; thermalizer/commercialized; coated insert
13. Application/stage	Diamond semiconductor; optical substrate for IC; window for IC;
15. Comments on status/areas requiring work/applications	Diamond laser; wear-resistant parts; electronics heat sinks; FEI

TABLE A-2. Survey Response Data Tabulation (1 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Applied Science & Technology, Inc.

Dr. Richard S. Post, Ph.D

January 26, 1989

Lawrence Bourget, Richard S. Post, Donald K. Balta

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

Dr. Russell Messier, Pennsylvania State University
Dr. Michael Beiss, Lincoln Laboratories/Massachusetts Institute of Technology

Dr. Burton Meyerson, IBM/Yorktown

Yes

18. Use name?

19. Survey attachments

20. General discussion

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Asahi Diamond Industrial Co.

Fuimori Ohzumi, Chief Clerk

12-8-88

Fuimori Ohzumi

F. Ohzumi, "New Diamond", No. 1, P. 64, for overseas readers (1988)

"New Diamond", No. 9, P. 34, in Japanese (1988)

et al, Journal of the Japan Society of Powder and Powder Metallurgy, 35 (1988), 114

Two page note: "Gaseous Phase Synthesis of Diamond and its Practical Application"; Asahi Annual Report, 1988

Dr. Yoichiro Sato, National Institute for Research in Inorganic Materials

Yes

SURVEY RESPONSE DATA TABULATION

TABLE A-2. Survey Response Data Tabulation (2 of 14)

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Auburn University

Davidson, Dr. J.L.

12-20-88

Dr. T. Roppel, Dr. V. Izeng

SPIE, I-88, J.L. Davidson

no data

Hessler, Penn State; Maruyama, RTI; Peto, Stanford; Wollan, U. Nebraska; Matsuo, Japan; Matsuda, Japan; Brown, U. NC State

yes

Abstract: "Dielectric Properties of Carbon Films From Plasma Chemical Vapor Deposition", JLD & TMR (SPIE paper on order; new contacts)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

Individual responding

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

DEANALLOY CORPORATION

PUBLIN RESEARCH PARK

6360 DUBLIN INDUSTRIAL PARK

PURDUE, OHIO 43017

(614) 744-3300

Arnold H. Deutchman, Ph.D.

President

03 February 1989

Dr. Arnold H. Deutchman, Mr. Robert J. Parteka, Mr. J. Clifford Lewis.

Arnold H. Deutchman, Ph.D.

See attached.

See attached.

a. Richard Post, Applied Science and Technology, Newton, MA.

b. K. V. Ravi, Crystallume, Menlo Park, CA.

c. David Hoover, Air Products and Chemicals, Allentown, PA.

d. Irwin Singer, Naval Research Laboratories, Washington, D.C.

e. John Angus, Case Western Reserve University, Cleveland, OH.

18. Use name?

Yes

19. Survey attachments

Preprint Submitted to Journal of Metals, Deposition of Diamond Films on

Arnold H. Deutchman and Robert J. Parteka

DEANALLOY CORPORATION

Application and Utility of Industrial Diamond-Like Films

Arnold H. Deutchman and Robert J. Parteka

Excerpt from Industrial Heating - July 1988

BIOND

Hard Diamond Films from DeanAlloy

DeanAlloy/News Release

ION IMPLANTATION/ADVANCED TECHNOLOGIES FOR SURFACE ENGINEERING

20. General discussion

SURVEY RESPONSE DATA TABULATION

TABLE A-2. Survey Response Data Tabulation (3 of 14)

INSTITUTION:

Case Western Reserve University, Case Institute of Technology

School of Engineering

Chemical Engineering Department

Cleveland, Ohio 44106 (216) 368-4180

John C. Angus, Professor of Engineering

03 February 1989

Prof. John C. Angus, Prof. Richard W. Hoffman, Prof. Benjamin Segall, Dr. Walter Lambrecht, Mr. Cliff C. Hayman, Mr. Theodore Broth,

Mrs. Virginia Jeffers, Mr. Mahendra Anandara, Mr. Hsiung Chen, Mr. Yasia Wang,

Refer to question 19.

Refer to question 19.

Dr. Robert Clausen, Oak Ridge National Labs, Dr. Stephen Harris, General Motors,

Dr. Frank Jansen, Iseron, Dr. Paul Schmitt, DEC.

May

See attachment

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Crystalline

Michael pinneo

5-8-89

M. Peters, L. Plano, K.V. Ravi, M. Landstrass, J. Herb, M. Planco, J. Knowles, C. Bailey

See list

See package

TABLE A-2. Survey Response Data Tabulation (4 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

David Sarnoff Research Center

Dr. Aaron Levine

1-3-89

Mr. Yehuda Arie, Mr. Ormond A. Mester, Dr. Bawa Singh

Four reprints/preprints enclosed

Brochure enclosed

See list of SRI/DOST and NBS meetings

yes

Singh, Arie, Levine and Mester, 2/88; Singh, Mester, Levine and Arie, 1988; Singh, Mester, Levine and Arie, 5/88; Singh, Mester, Levine and Arie, preprints; brochure

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

18. Use name?

19. Survey attachments

20. General discussion

Diamond Materials Institute, Inc.

2820 East College Avenue

State College, PA 16801 (814) 231-6200 FAX: (814) 237-1186

Dr. Richard Koba

06 February 1989

Richard Koba, Ph.D., Donald Kupp, Andrew Phelps

See items 10 & 13.

(1) "P-type Diamond Stripper Foils for Tandem Ion-Accelerators," to be presented at Electrochemical Society Meeting, May 1989.

(2) "Heterogeneous Nucleation of Diamond Powder in the Gas Phase," manuscript submitted to J. App. Phys.

6. iribological applications of diamond films: how to improve film adhesion to a variety of substrates.

None

Yes

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active ind: also

16. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Fujitsu Laboratories, Ltd.

Dr. Motonobu Kawanada, Senior Researcher, Functional Materials Laboratory

12-4-88

Dr. Motonobu Kawanada, Mr. Kazuaki Kurihara, Mr. Nagasaki Koshino

K. Kurihara, K. Sasaki, H. Kawanada, and M. Koshino, Appl. Phys. Lett. 52(6), 437 (1988).

M. Koshino, K. Kurihara, H. Kawanada and K. Sasaki, Extended Abstracts Diamond and Diamond-Like Materials Synthesis, MSB, 95 (1988)

H. Kawanada, K. Kurihara, K. Sasaki, A. Teshima and M. Koshino, First Inter. Conf. on the New Diamond Science and Tech., Tokyo, 42 (1988)

Included

Dr. Masanori Yoshikawa, Prof. Tokyo Inst. of Tech.

Yes

Laboratory descriptive brochure

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

Idemitsu Petrochemical Co., Ltd

Kazuaki Ito, Manager, High Tech. Materials

1-27-89

Akio Hirayama, Toshioichi Ito, Maruyuki Hayashi

Dr. Setaka, Dr. Sato, Dr. Kano, Dr. Matsumoto, Dr. Moritoshi, National Research Laboratory, Inorganic Materials, Tsukuba

Yes

Article from Chemistry Letters; Company profile

TABLE A-2. Survey Response Data Tabulation (6 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:
Individual responding
Response date
1. Active individuals
14. Reports
16. Descriptive literature on organization
17. Other researchers who should be contacted
18. Use name?
19. Survey attachments
20. General discussion

SURVEY RESPONSE DATA TABULATION

INSTITUTION:
Individual responding
Response date
1. Active individuals
14. Reports
16. Descriptive literature on organization
18. Use name?
19. Survey attachments
20. General discussion

TABLE A-2. Survey Response Data Tabulation (7 of 14)

SURVEY RESPONSE DATA TABULATION	INSTITUTION:	DEPARTMENT OF THE NAVY	16. Descriptive literature on organization
		NAVAL RESEARCH LABORATORY	
Individual responding	Response date	CODE 6174	17. Other researchers who should be contacted
		WASHINGTON, D.C. 20375-5000	
1. Active individuals	J. E. Butler	J.E. Butler	18. Use name?
		22 January 1989	
19. Survey attachments	J. E. Butler	J. E. Butler	19. Survey attachments
		B. B. Oakes, C. B. Pande, C. L. Vold, H. Hoff, P.H. Klein, U. Strom, J. Fritter, K. Slegner, A. Morriah.	
20. General discussion	J. E. Butler	B. B. Oakes, C. B. Pande, C. L. Vold, H. Hoff, P.H. Klein, U. Strom, J. Fritter, K. Slegner, A. Morriah.	20. General discussion
		J.E. Butler	
SURVEY RESPONSE DATA TABULATION	INSTITUTION:	DEPARTMENT OF THE NAVY	16. Descriptive literature on organization
		NAVAL RESEARCH LABORATORY	
Individual responding	Response date	CODE 6174	17. Other researchers who should be contacted
		WASHINGTON, D.C. 20375-5000	
1. Active individuals	J. E. Butler	J.E. Butler	18. Use name?
		22 January 1989	
19. Survey attachments	J. E. Butler	J. E. Butler	19. Survey attachments
		B. B. Oakes, C. B. Pande, C. L. Vold, H. Hoff, P.H. Klein, U. Strom, J. Fritter, K. Slegner, A. Morriah.	
20. General discussion	J. E. Butler	B. B. Oakes, C. B. Pande, C. L. Vold, H. Hoff, P.H. Klein, U. Strom, J. Fritter, K. Slegner, A. Morriah.	20. General discussion
		J.E. Butler	

TABLE A-2. Survey Response Data Tabulation (8 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

18. Use name?

19. Survey attachments

20. General discussion

Mortco Christensen, Inc., Diamond Technology Center

25325 South 3270 West

Salt Lake City, Utah 84119

Dr. L.K. Bigelow

26 January 1989

Dr. L.K. Bigelow, Dr. J.I. Higgins, and staff

Borohoe Conference, Monterey Co., Fall 1988, Presented by Ray Becker.

None available

Yes

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Osaka Diamond Industrial Co., Ltd.

N. Tsubota, Manager, R&D

2-6-89

N. Tsubota, K. Nishimura, Kazuhito

N. Kawanada, et al "Blue and Green Cathodoluminescence of Synthesized Diamond Films Formed By Plasma-assisted Chemical Vapor Deposition"

Japan Journal of Applied Physics, Vol. 27, No. 4, April, 1988, pp 483-486

Company brochure and 1987 financial statement

Dr. A. Mirzai, Dept of Electrical Engineering, Osaka Univ.

Yes

TABLE A-2. Survey Response Data Tabulation (9 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Shima Dento K. K. Central Research Lab
Kusio Kosaki, Research Manager, Key Technology Development Division

12-6-88

Dr. Kusio Kosaki

N. Yanagisawa, K. Kosaki, et al., "Extended Abst. of J. Appl. Phys. 35th Meeting, 1989. 2, 434 (1989)

K. Kosaki, et al., First Int. Conf. on Diamond, extended abstract, p 112 (1989)

K. Kosaki, et al., New Diamond 4, p23 (1989)

Y. Hirose, K. Kosaki, First Inter. Symp. on Diamond Ab. Eco extended Abstract (1989) To be presented
Brochure and annual report, 1987. One of the leading chemical companies in Japan.

Products range from petrochemical products to metals, inorganic goods, ceramics, CDM, diamond, etc.

SURVEY RESPONSE DATA TABULATION

INSTITUTION

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use name?

19. Survey attachments

20. General discussion

Saito Electric Industries, Ltd.

A. Nishikawa, Development planning Dept, R&D Group

12-6-88

Dr. Masaji Fujimori

Fujimori, M. T/ Inal and A. Bol, "Characterization of Conductive Diamond Film", Vacuum, Vol 36, No. 1-3, 99(1986)

Fujimori, M. "Application of Diamond Film or Diamond-like Carbon Film Coating to Blaphrage", New Diamond, p 36 (1989)

Brochure and annual report (1988)

Yochiro Seta, Nat. Inst. for Research in Inorganic Materials Michio Inoue, Professor, Univ. of Aoyama-gakuin

Yes

TABLE A-2. Survey Response Data Tabulation (10 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:
TEXAS INSTRUMENTS
DALLAS, TEXAS 75115
A.J. PUMPER
12 January 1989
A.J. PUMPER

- Individual responding
Response date
1. Active individuals
14. Reports
16. Descriptive literature on organization
18. Use name?
19. Survey attachments
20. General discussion

Yes
None

SURVEY RESPONSE DATA TABULATION

INSTITUTION:
Tokyo University of Agriculture
Dr. A. Koike
2-20-89
Minoru Koike
Paper in preparation
University brochure

- Individual responding
Response date
1. Active individuals
14. Reports
16. Descriptive literature on organization

H. Betsko and Y. Sato, National Inst. for Research of Inorganic Materials
Y. Hirose, Nippon Inst. of Tech.
Yes

17. Other researchers who should be contacted
18. Use name?
19. Survey attachments
20. General discussion

TABLE A-2. Survey Response Data Tabulation (11 of 14)

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

Toshiba Corp.

Atsuhiko Sasebe, Researcher, R&D Center

12-4-80

A. Sasebe and T. Inuzuka, Appl. Phys. Lett. 46, 146 (1985)

A. Sasebe and T. Inuzuka, Thin Solid Films. 137, 89 (1986)

K. Suzuki, A. Sasebe, H. Yasuda and T. Inuzuka, Adv. Phys. Lett., 50, 720 (1987)

A. Sasebe, H. Yasuda, T. Inuzuka and K. Suzuki, Appl. Sur. Sci., 33/34, 539 (1988)

H. Kaneko, M. Kanada, R. Kusan, A. Sasebe, and T. Inuzuka, Appl. Sur. Sci., 33/34 546 (1988)

K. Suzuki, A. Sasebe, and T. Inuzuka, Appl. Phys. Lett., 53, 1818 (1988)

A. Sasebe, Trans. IEE of Japan, 106-A, 179 (1986) (in Japanese)

T. Inuzuka and A. Sasebe, OYO BUTURI, 55, 640 (1986) (in Japanese)

A. Sasebe and T. Inuzuka, J. IEE of Japan, 106, 1211 (1986) (in Japanese)

Toshiba Review (periodic publication); A guide to Toshiba Research and Development Center

16. Descriptive literature on organization

17. Other researchers who should be contacted

Dr. Yoichiro Sato, National Inst. for Research in Inorganic Matls.; Dr. Yoichi Hirose, Nippon Inst of Tech.; Prof. Akio Hirah, Osaka Univ.; Prof. Osamu Matsumoto, Aoyama Gakuin Univ.

SURVEY RESPONSE DATA TABULATION

INSTITUTION:

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

17. Other researchers who should be contacted

18. Use axes?

19. Survey attachments

20. General discussion

Tottori University

Mr. K. Nishimori and Mr. H. Tototake, Associate Prof.

12-4-80

H. Tototake, K. Nishimori, S. Kishida, and M. Ishihara, Dept of Electronics

"Growth of Diamond Thin Films Using A Simple Microwave Plasma CVD Apparatus" to be published in J. of Vacuum Soc. of Japan

Brochure on Tottori University

Yes

SURVEY RESPONSE DATA TABULATION

TABLE A-2. Survey Response Data Tabulation (12 of 14)

INSTITUTION

Individual responding

Response date

1. Active individuals

14. Reports

16. Descriptive literature on organization

18. Use name?

19. Survey attachments

20. General discussion

WAYNE STATE UNIVERSITY/ INSTITUTE FOR MANUFACTURING RESEARCH, DIAMOND AND DIAMOND LIKE MATERIALS

Dr. Richard W. Pryor

02-14-89

Principal Investigator: R. W. Pryor and Students. Others Collaborate.

We are just beginning to publish our results on diamond. No paper in print, yet.

See Attachment

Yes

Description of Wayne State University Materials Research Laboratory

TABLE A-2. Survey Response Data Tabulation (13 of 14)

**RECENT PUBLICATIONS ON CVD DIAMOND
AND DIAMONDLIKE FILMS**

John C. Angus
Department of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106

JOURNAL ARTICLES AND BOOK CHAPTERS

1. John C. Angus, Michael J. Mirtich and Edwin G. Wintucky, "Ion Beam Deposition of Amorphous Carbon Films with Diamondlike Properties," in *Metastable Materials Formation by Ion Implantation*, S.T. Picraux and W.J. Choyke, editors, Elsevier Science Publishing Co., pp. 433-40, 1982.
2. John C. Angus, Janet E. Stultz, Paul J. Shiller, Jack R. McDonald, Michael J. Mirtich and Stan Domitz, "Composition and Properties of the So-Called 'Diamondlike' Amorphous Carbon Films," Thin Solid Films, 118, 311-20 (1984).
3. Michael J. Mirtich, Diane M. Swec and John C. Angus, "Dual-Ion-Beam Deposition of Carbon Films with Diamond-Like Properties," Thin Solid Films, 131, 245-254 (1985).
4. John C. Angus, "Empirical Categorization and Naming of 'Diamondlike' Carbon Films," Thin Solid Films, 142(1) 145-51 (1986).
5. John C. Angus, Peter Koidl and Stanley Domitz, "Dense Carbonaceous Films with 'Diamondlike' Properties," chapter 4 in "Plasma Deposition of Thin Films," J. Mort and F. Jansen, eds., CRC Press, Boca Raton, FL, pp 89-127 1986.
6. John C. Angus and Frank Jansen, "Dense 'Diamondlike' Hydrocarbons as Random Covalent Networks," J. Vac. Sci. and Tech. A 6(3), 1778-82, May/June 1988.
7. John C. Angus and Cliff Hayman, "Low Pressure Growth of Diamond and 'Diamondlike' Phases," Science 241, 913-921 (1988).

SYMPOSIA AND CONFERENCE PROCEEDINGS

8. John C. Angus, "Some Aspects of the Growth and Characterization of Diamondlike Carbon Films," in *Proceedings of the DARPA Workshop on Diamondlike Carbon Coatings*, Bernard BendoW, editor, Albuquerque, NM, April 19-20, 1982.
9. John C. Angus, "Plasma Deposition of the So-Called 'Diamondlike' Hydrocarbon and Carbon Films," NSF Workshop on "The Plasma, Ion and Laser Assisted Chemical Processing of Electronic Materials," San Diego, CA, February 23, 1987.
10. John C. Angus, "Categorization of Dense Hydrocarbon Films," invited paper, European Materials Research Society Meeting, Strasbourg, France E-MRS Vol. XVII, 179-187 (1987),

TABLE A-2. Survey Response Data Tabulation (14 of 14)

11. John C. Angus, "Dense 'Diamondlike' Hydrocarbon and Carbon Films," invited paper, Second Annual Department of Defense Diamond Technology Initiative Seminar, Durham, NC, July 7-8, 1987.
12. John C. Angus, "Formation of Diamondlike Films," invited plenary lecture, XVIIIth Biennial Conference on Carbon, Worcester, MA, July 22, 1987.
13. John C. Angus, "Dense 'Diamondlike' Hydrocarbon and Carbon Films," Conference on Emerging Technologies in Materials, AIChE National Meeting, Minneapolis, August 18, 1987.
14. John C. Angus, "Dense Hydrocarbon Solids: A New Material with 'Diamondlike' Properties," Invited paper, American Vacuum Society Meeting, Anaheim, CA, November 2-6, 1987.
15. John C. Angus, Richard W. Hoffman and Kevin Chaffee, "Secondary Elements in a-C:H," Materials Research Society Meeting, Boston, MA, December 2, 1987.
16. John C. Angus, invited plenary lecture, "Diamond and 'Diamondlike' Thin Films: Synthesis at Low Pressure and Applications," The Diamond Conference, Cambridge University, July 7, 1988.
17. John C. Angus, "Growth Studies of Diamond and 'Diamondlike' Phases," Diamond Technology Initiative Symposium, July 12-14, 1988, Arlington, VA.
18. John C. Angus, invited lecture, "Diamond and 'Diamondlike' Phases," Proceedings of the 32nd Annual International Technical Symposium on Optical and Optoelectronic Applied Science and Engineering (SPIE), San Diego, CA, August 14-19, 1988.
19. John C. Angus, "Diamond and 'Diamondlike' Coatings," Proceedings of World Materials Congress, ASM, Chicago, September 24-30, 1988.
20. John C. Angus, invited lecture, "Studies of Amorphous Hydrogenated 'Diamondlike' Hydrocarbons and Crystalline Diamond," Proceedings of First International Conference on the New Diamond Science and Technology, Tokyo, October 24-26, 1988.

APPENDIX B

EVALUATION OF DIAMOND FILM
STRENGTH CALCULATIONS

TO: D. M. Jassowski 17 April 1989
FROM: B. P. Beaudette 8PB:gg:9982:3968
SUBJECT: Evaluation of Diamond Film Strength Calculations
COPIES TO: J.W. Salmon, 9982 File
ENCLOSURE: (1) Evaluation of Diamond Film Strength
Calculations
(2) Interfunction Secondary Authorization

The ultimate tensile strength of diamond film is evaluated in Enclosure (1) using two theories. Plate and plate large deflection theory are used. This analysis indicates that plate theory is not appropriate to use when estimating the film's tensile strength. Plate large deflection theory is more appropriate. This theory indicates that the tensile stress in the film, at maximum pressure, is 250,000 psi. This value is 1/12th that predicted by plate theory.

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ENCLOSURE (1)

EVALUATION OF DIAMOND FILM
STRENGTH CALCULATIONS

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STRUCTURAL ANALYSIS REVIEW FORM

DATE: April 12, 1989

PROGRAM: Diamond Film

COMPONENT: —

PURPOSE of ANALYSIS: Determine if flat plate analysis is appropriate.
If it is not, what is the magnitude of error.

ANALYSIS PROGRAM & VERSION:
TAPE SAVE SET & FILE NAMES:

Hand calculations

MATERIALS: (Material Name)

1. Diamond Film
- 2.
- 3.

VALUE OR PAGE NUMBER	INFORMATION SOURCE	APPROVAL
$E = 170 \times 10^6 \text{ psi}$	K	
$\nu = 0.20$		

LOADS & TEMPERATURE:

1. PRESSURE
 - a. Steady State
 - b. Transient
2. TEMPERATURE DISTRIBUTION
 - a. Steady State
 - b. Transient
3. THRUST AND THRUST TRANSIENT
4. ACCELERATION
5. VIBRATION
6. ACOUSTIC
7. LOAD HISTORY

63.1 psi

K

GEOMETRY AND PHYSICAL CHARACTERISTICS:

1. Dimensions
2. Boundary Conditions
3. Weights and Masses
4. Stiffness

Page 3

K

INFORMATION SOURCE LEGEND:

- A. Mil Hdbk 5
- B. Rep. MA-81-107
- C. Specs 1. _____
2. _____ 3. _____
- D. Drawings 1. _____
2. _____ 3. _____
- E. Reports 1. _____
2. _____ 3. _____

- F. Verbal _____
- G. Estimate _____
- H. Calculated _____
- I. Layout _____
- J. Lab Tests _____
- K. Provided by Crystallume (Contractor)
- L. _____
- M. _____

APPENDIX B

INTRODUCTION

The following analysis was prepared to critically review data obtained from previous studies which indicated diamond film tensile strengths of 3×10^6 psi. These data were obtained during routine proof testing of x-ray windows in which occasional specimens were pressurized to burst.

The calculated stresses at failure, based on plate theory, were 3 to 6×10^6 psi. As shown in the analysis, membrane theory must be applied because of the geometry of the specimen, so the calculated stress at failure is much lower.

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II. Summary of Results	B-7
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B-2 View of the Specimen, Looking Down from Above	B-11
B-3 Normalized Stress vs. Pressure	B-16
B-4 Normalized Deflection vs. Pressure	B-17

REFERENCES

1. Raymond J. Roark, and Warren C. Young, "Formulas for Stress and Strain", 5th Edition
2. Murray R. Spiegel, "Schaum's Outline Series, Mathematical Handbook of Formulas and Tables", Copyright 1968

I. INTRODUCTION

This report was prepared for the Research Department on the material properties of diamond film. The purpose of this report is to determine if the tensile strengths of samples of diamond film are being properly estimated. If these estimates are being calculated incorrectly, then a second purpose of this report is to estimate the magnitudes of the errors.

The test specimens consist of a thin diamond film (1.6×10^{-5} inches thick) deposited on a silicon wafer. This wafer then has long, narrow slots etched into it, leaving columns of silicon to support the diamond film. The finished test specimen has pressure applied to it until it fails. The pressure at which failure occurs is then used to estimate the tensile strength of the diamond (previously using flat-plate theory). Figure B-1 is a schematic of the test specimens.

II. SUMMARY OF RESULTS

The ultimate tensile strengths and maximum panel deflections are shown below. They have been calculated by Plate Theory and Plate large deflection theory. Plate theory assumes deflections are small (on the order of $1/2$ the panel thickness). Large deflection theory takes both bending and membrane stresses into account. Neither the bending nor shear stresses, at supports, are taken into account in this analysis.

Input to this Analysis:

Applied Pressure: 64.1 psi

Panel Thickness: 1.6×10^{-5} in.

Panel Width: 0.004 in.

Panel Length/Width Ratio: ∞

Diamond Modulus of Elasticity: 170×10^6 psi

Diamond Poisson's Ratio: 0.2

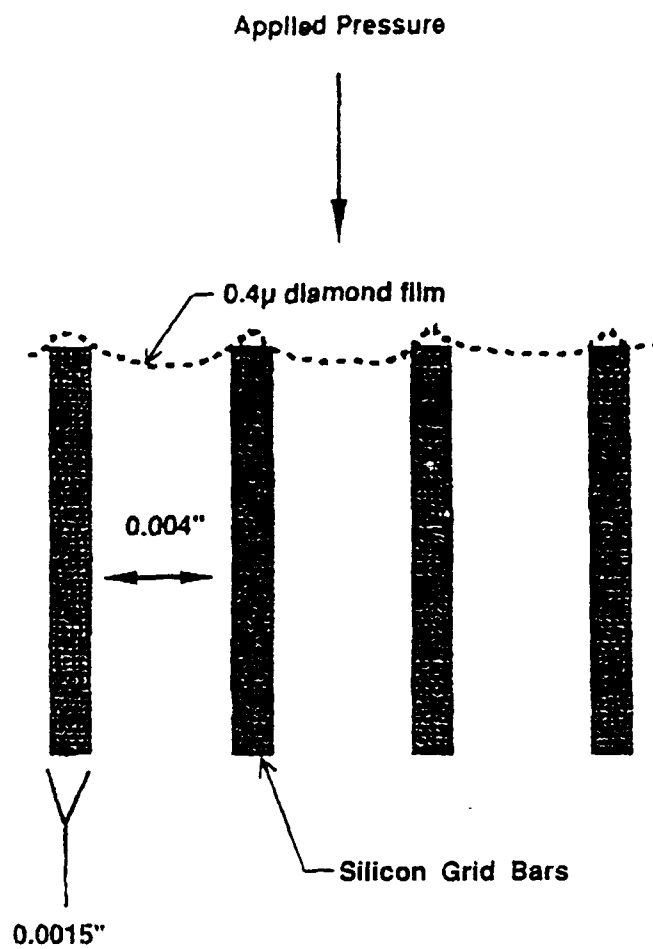


Figure B-1. Schematic of Test Specimen Cross-Section
(End View).

Flat Plate Theory Results:

$$\sigma_{\max} = 3.005 \times 10^6 \text{ psi}$$

$$y_{\max} = 0.00335 \text{ in.}$$

$$\frac{y_{\max}}{t} = 209.3$$

Plate Large Deflection Theory

$$\sigma_{\max} = 250,000 \text{ psi}$$

$$y_{\max} = 0.00010 \text{ in.}$$

$$\frac{y_{\max}}{t} = 6.358$$

III. CONCLUSIONS AND RECOMMENDATIONS

It is concluded that flat plate theory should not be used to estimate the stresses in these diamond film specimens. The theory's results are not valid for a film which has a deflection-to-thickness ratio as large as this does. It is concluded that the strength estimates from flat plate theory are possibly 12 times too high (membrane theory gives a maximum stress at failure 1/12th of the stress from flat plate theory).

An important point needs to be made: The large deflection theory may be accurately estimating the axial stress in the film, at the specified pressure. But, this may not be the failure mechanism of the specimens. Some other mechanism may be causing the specimens to fail. For example, the film may be failing in shear, or the supports (silicon grids) may be failing.

If it is anticipated that this type of specimen will continue to be used, then its failure mechanisms must be clearly understood. A preferable path would be to develop a specimen specifically designed to evaluate the mate-

rial properties of interest. For example, if tensile strength is of interest, create a tensile pull specimen.

IV. TEST SPECIMEN TEST DATA

A. LOADS

The specimen being analyzed failed at a pressure of 64.1 psi.* This specimen had the film floated onto the silicon gridwork. This means that the diamond is not permanently bonded onto the grids.

B. MATERIAL PROPERTIES OF DIAMOND FILM*

$$E = 170 \times 10^6 \text{ psi}$$

$$\nu = 0.2$$

The tables in Reference (1) use a Poisson's Ratio of 0.3. These tables are used directly, in this analysis. It is assumed that the error is small (see page 385 of Reference 1). Linear behavior to failure is assumed in this analysis--no plasticity.

V. ANALYSIS

A. GEOMETRY AND PHYSICAL CHARACTERISTICS

Figure B-1 shows a cross-section of the test specimen. Below is a sketch of the diamond film to be analyzed, Figure B-2..

Figure B-2, is a view of the Specimen, Looking Down From Above

* Provided by Crystallume

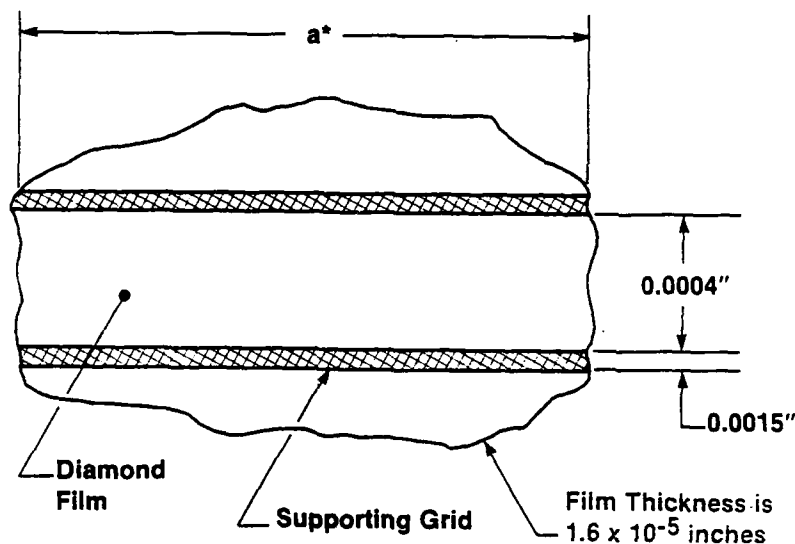


Figure B-2. View of the Specimen, Looking Down from Above.

B. METHOD OF ANALYSIS

Initial estimates of the tensile strength of diamond film have been made assuming that the film acts as a plate. This analysis has assumed that the film was a rectangular plate, uniformly loaded, and simply supported.

The flat plate analysis is repeated in this report. It is also shown in this report that this type of analysis is incorrect for this type of test specimen.

A large-deflection analysis is also presented in this report. The results from this analysis suggest that it is a more accurate estimation of strength, because panel deflections are more reasonable.

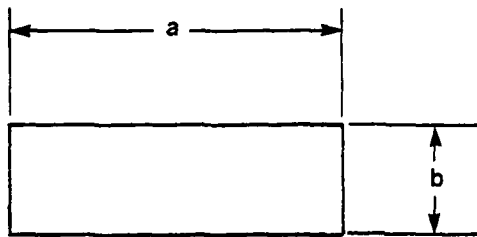
C. STRENGTH ESTIMATE BASED UPON PLATE THEORY

All equations used in this analysis are from Reference B-1 (Roark, 5th ed., Case 1a, Table 26, page 386).

This analysis assumes that the film is a rectangular diaphragm, uniformly loaded, and simply supported.

This analysis assumes that

$$a/b \Rightarrow \infty, \text{ and therefore } \beta = 0.7500$$



$$b = 0.004''$$

$$t = 1.6 \times 10^{-5} \text{ inches}$$

$$E = 170 \times 10^6 \text{ psi}$$

$$\nu = 0.2$$

Pressure = 64.1 psi
at failure

1. Calculate the Maximum Stress

$$\sigma_{\max} = 0.75 \frac{Pb^2}{t^2} = 0.75 (64.1) \frac{(0.004)^2}{(1.6 \times 10^{-5})^2}$$

$$\sigma_{\max} = 3.005 \times 10^6 \text{ psi}$$

2. Calculate the Maximum Deflection

$$y_{\max} = \frac{-\alpha (P) b^4}{Et^3}$$

Assuming $\frac{a}{b} = \infty$, and $\nu = 0.30$, the table in Reference 1 gives

$$\alpha = 0.1421$$

$$y_{\max} = \frac{-(0.1421) (64.1 \text{ psi}) (0.004 \text{ in})^4}{(170 \times 10^6 \text{ psi}) (1.6 \times 10^{-5} \text{ in})^3}$$

$$y_{\max} = 0.00335 \text{ in}$$

Flat-plate theory holds as long as the maximum deflection is less than one-half the plate thickness (see pages 405-406 of Reference B-1). In this analysis, the maximum deflection is 209 times the plate thickness.

$$\frac{y_{\max}}{t} = \frac{0.00335 \text{ in}}{1.6 \times 10^{-5} \text{ in}}$$

$$\frac{y_{\max}}{t} = 209.4$$

The calculated deflection is far beyond the limits of the theory. Therefore, plate theory is not the correct theory to use when estimating the stresses in the diamond film.

D. STRENGTH ESTIMATE BASED UPON LARGE DEFLECTION THEORY

The table on page 408 of Reference (B-1) is used to estimate the stress and deflection of the diamond film. In this table, the parameter $\frac{qb^4}{Et^4}$ has an upper limit of 250.

In this analysis, this parameter has a much higher value.

$$\frac{Pb^4}{Et^4} = \frac{(64.1 \text{ psi}) (0.004 \text{ in})^4}{(170 \times 10^6 \text{ psi}) (1.6 \times 10^{-5} \text{ in})^4}$$

$$\frac{Pb^4}{Et^4} = 1473$$

In order to account for the fact that this problem is off the scale of Reference B-1, the table on page 408 was plotted and linearly extrapolated.

The table is reproduced on the next page as Table B-1 while the curves are shown in Figures B-3 and B-4. Using a linear extrapolation may be non-conservative, but a goal of this analysis is to estimate the magnitude of error when a plate analysis is used. Using a linear extrapolation gives a minimum, and thus optimistic, magnitude of error.

1. Extrapolate the Film Stress

Figure A-3 is used in this analysis

Slope of linear portion of curve = m

$$m = \frac{\Delta y}{\Delta X} = \frac{\frac{\Delta \sigma b^2}{Et^2}}{\frac{\Delta qb^4}{Et^4}} = \frac{23.6 - 18.0}{250 - 150}$$

$$m = 0.056$$

$$\text{Let } y = \frac{\sigma b^2}{Et^2}, x = \frac{qb^4}{Et^4}$$

$$y - y_0 = m (x - x_0)$$

$$y - 23.6 = 0.056 (1473 - 250)$$

$$y = 92.09$$

$$\frac{\sigma b^2}{Et^2} \approx 92$$

$$\sigma \approx \frac{92 (170 \times 10^6 \text{ psi}) (1.6 \times 10^{-5} \text{ in})^2}{(0.004 \text{ in})^2}$$

$$\boxed{\sigma \approx 250,000 \text{ psi}}$$

TABLE B-1. From Page 408 of Reference 1

Rectangular plates under uniform load producing large deflection

a/b	Edges and points of max σ	Coef.	qb^4/Et^4										
			0	12.5	25	50	75	100	125	150	175	200	250
1	Held, not fixed	$\gamma/1$	0	0.430	0.650	0.930	1.13	1.26	1.37	1.47	1.56	1.63	1.77
	At center of plate	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	0.70	1.60	3.00	4.00	5.00	6.10	7.00	7.95	8.60	10.20
1	Held and riveted	$\gamma/1$	0	0.406	0.600	0.840	1.00	1.13	1.23	1.31	1.40	1.46	1.58
	At center of plate	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	0.609	1.380	2.68	3.80	4.78	5.75	6.54	7.55	8.10	9.53
1	Held and fixed	$\gamma/1$	0	0.165	0.25	0.59	0.80	0.95	1.08	1.19	1.28	1.38	1.54
	At center of long edges	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	0.070	0.22	0.75	1.35	2.00	2.70	3.30	4.00	4.60	5.90
1.5	At center of plate	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	3.80	6.90	14.70	21.0	26.50	31.50	36.20	40.70	45.00	53.50
	Held, not fixed	$\gamma/1$	0	0.625	0.879	1.18	1.37	1.53	1.68	1.77	1.88	1.96	2.12
2	At center of plate	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	1.06	2.11	3.78	5.18	6.41	7.65	8.60	9.55	10.60	12.30
	Held, not fixed	$\gamma/1$	0	4.48	6.81	9.92	12.25	14.22	16.0	17.50	18.90	20.30	22.80
2	At center of plate	$\gamma/1$	0	0.696	0.946	1.24	1.44	1.60	1.72	1.84	1.94	2.03	2.20
	Held and fixed	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	1.29	2.40	4.15	5.61	6.91	8.10	9.21	10.10	10.90	13.20
2	At center of plate	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	4.87	7.16	10.30	12.60	14.60	16.40	18.00	19.40	20.90	23.60
	Held and fixed	$\gamma/1$	0	0.28	0.51	0.825	1.07	1.24	1.40	1.50	1.63	1.72	1.86
2	At center of long edges	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	0.20	0.66	1.90	3.20	4.35	5.40	6.50	7.50	8.50	10.30
	Held and fixed	$\frac{\sigma_x b^2/Et^2}{\sigma_y b^2/Et^2}$	0	5.75	11.12	20.30	27.8	35.0	41.0	47.0	52.50	57.60	67.00

Range Used in This Analysis

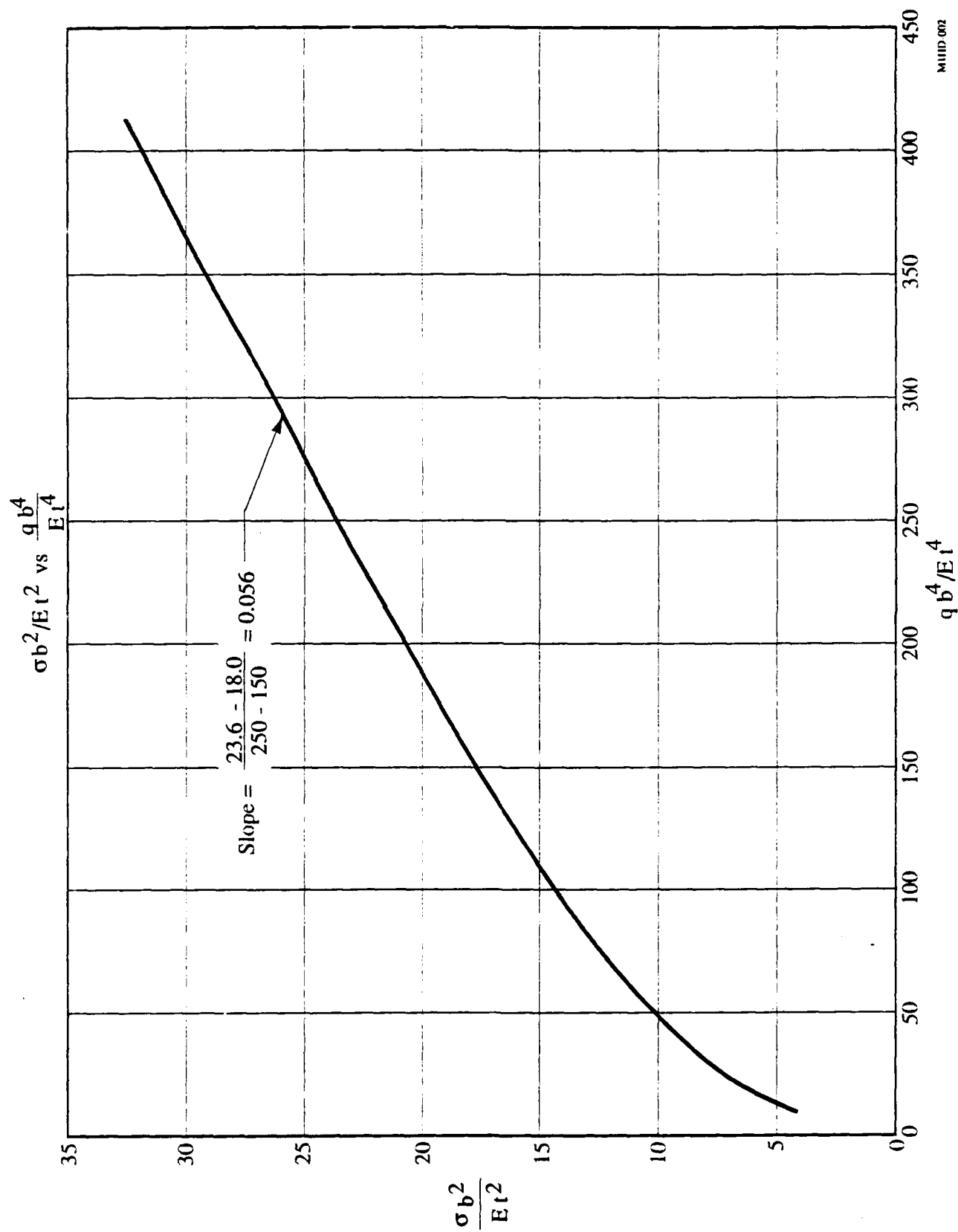


Figure B-3. Normalized Stress vs. Pressure.

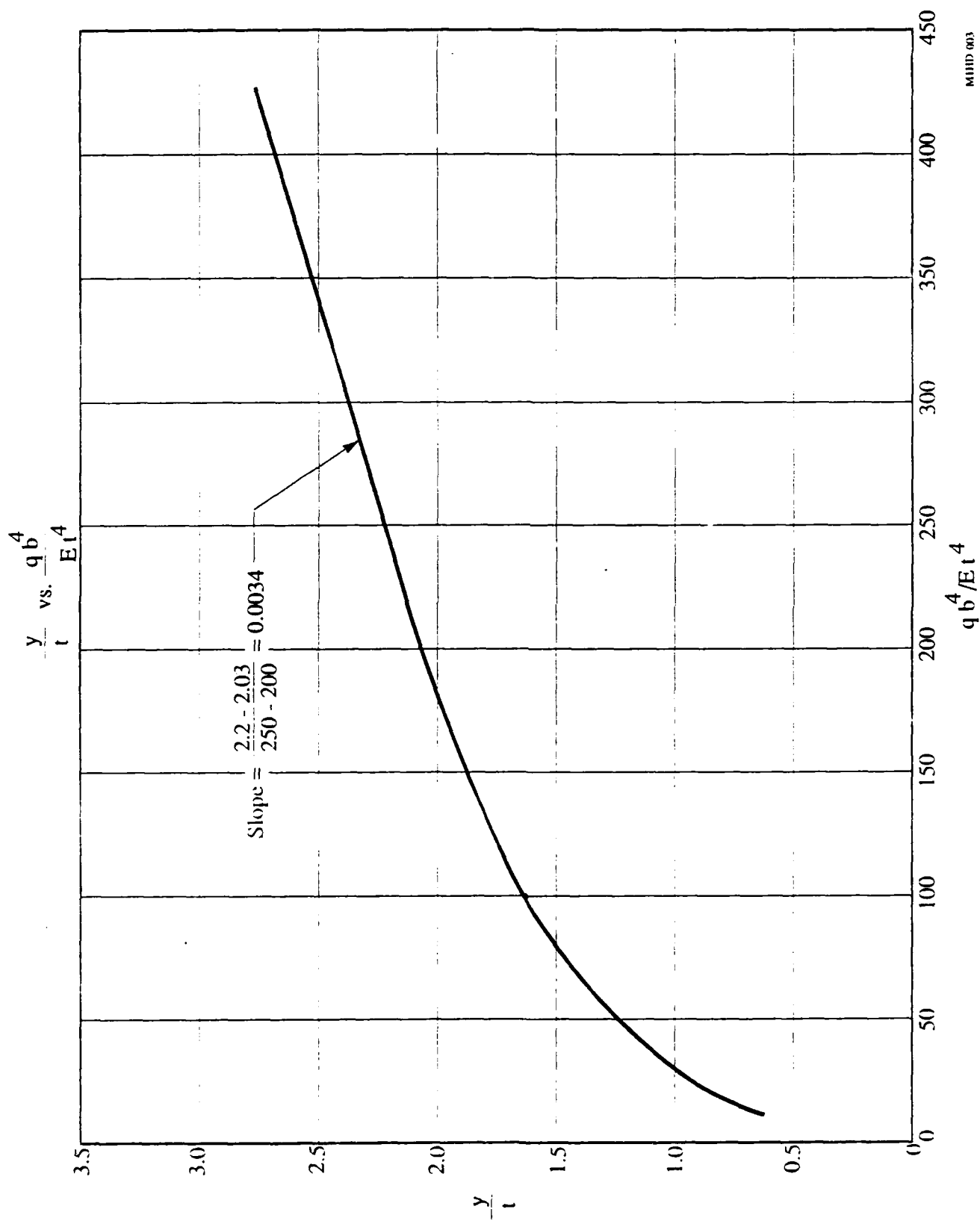


Figure B-4. Normalized Deflection vs. Pressure.

This estimation of film axial stress is approximately 12 times smaller than the estimation from flat plate theory.

2. Extrapolate the Maximum Deflection

Using Figure A-4, the maximum film deflection is calculated in the same manner as the film stress.

$$\text{Let } Z = \frac{y}{t}, x = \frac{qb^4}{Et^4}$$

$$Z - Z_0 = m (x - x_0)$$

$$m = \frac{\Delta Z}{\Delta X} = \frac{2.2 - 2.03}{250 - 200}$$

$$m = 0.0034$$

$$Z - 2.2 = 0.0034 (1473 - 250)$$

$$Z = 6.358$$

$$\frac{y}{t} = 6.358$$

$$y = 6.358 (1.6 \times 10^{-5} \text{ in})$$

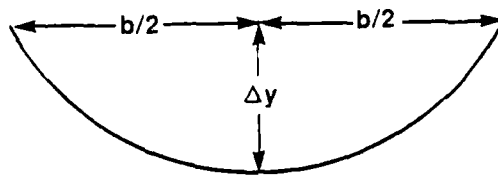
$$y_{\max} = 0.00010 \text{ in}$$

The maximum deflection is approximately 6.4 times the film thickness when large deflection theory is used.

3. Check the Large Deflection Results

By using the maximum deflection of the film, and assuming it deflects into a parabolic curve, the average strain can be estimated. Using this strain value along with the calculated stress, the modulus can be calculated. If this modulus is the same as the given modulus, then the stress and deflection calculations are somewhat validated.

Reference (2) provides an equation of the length of a parabola. This equation is used here to estimate the change in length of the diamond film.



$$b = 0.004''$$

$$\Delta y = 0.00010''$$

$$\text{Arc Length} = \frac{1}{2} [b^2 + 16 (\Delta y)^2]^{1/2} + \frac{b^2}{8\Delta y} \ln \left[4\Delta y + \frac{[b^2 + 16 (\Delta y)^2]^{1/2}}{b} \right]$$

$$\text{Arc Length} = 0.004006657$$

$$\text{Strain} = \frac{\Delta l}{l}$$

$$\epsilon = \frac{0.004 - 0.004006657}{0.004}$$

$$\epsilon = 0.00166 \text{ in/in}$$

Now calculate the modulus:

$$E = \frac{\sigma}{\epsilon}$$

$$E = \frac{250,000 \text{ psi}}{0.00166 \text{ in/in}}$$

$$E = 150 \times 10^6 \text{ psi}$$

This estimated value of elastic modulus is approximately 13% less than the given value of 170×10^6 psi. This relatively small difference suggests that the extrapolation of the tables in Reference (1) were appropriate. And that the stress estimate is a reasonable estimate of the maximum stress in the film.

APPENDIX C

DESIGN FOR CVD MONOLITHIC
DIAMOND PRESSURE VESSEL

APPENDIX C

DESIGN FOR CVD MONOLITHIC DIAMOND PRESSURE VESSEL

The following analysis was prepared to determine the feasibility of using a continuous CVD diamond film structure as a high-pressure vessel. Critical to the application is an acceptable transition from the CVD material to an attachment boss which makes the assembly into a practical pressure vessel. By an iterative process, the design was modified to nearly eliminate stress concentration at the attachment. However, detailed analysis of rupture test data indicated that the computed tensile strengths of 3×10^6 psi were actually perhaps a tenth of this. Subsequent rupture tests of more appropriated design specimens give tensile strengths of up to perhaps 0.7×10^6 psi. Many more measurements are required to give confidence in any of the values.

The CVD tank design is presented here as a potential future application for ultra-high strength CVD materials. The design is presented for a material with a tensile strength of 3×10^6 psi operating at a pressure of 25,000 psi; it is also appropriate for a material with a tensile strength of 700,000 psi operating at a pressure of 5,800 psi.

TO: D. K. Morgan 20 March 1989
LWB:gjo:9982:3916

FROM: L. W. Bush

SUBJECT: Diamond Tank Stress Results

COPIES TO: D.M. Jassowski, P.T. Lansaw, L. Schoenman,
J.R. Wooten, 9982 File

ENCLOSURE: (1) Subject Analysis

Recently, it has become possible to deposit thin films of diamond. Assuming it becomes possible to deposit relatively thick films and assuming this multi-crystalline film has a tensile strength similar to single crystal diamond, this then opens up a wide range of structural applications.

This analysis examined using diamond for a very light weight, very high pressure tank. The tensile strength used was 3.0×10^6 psi as per Deena Morgan.

Traditionally, pressure tanks are very over designed. The filler neck often causes a factor of 3.0 stress concentration. This analysis tried to optimize the filler neck shape and thickness variations to make the stress concentration as small as possible. The final model has a neck stress concentration of only 1.25.

Considering that only 3 days of effort went into this, this is a major accomplishment.

The design method for determining the weight of any chosen tank size and pressure are detailed in the conclusions.

L W Bush

L. W. Bush
Structural Analysis Section
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APPROVED BY:

J E Jellison

J. E. Jellison, Manager
Structural Analysis Section
Engineering Analysis Department

J W Salmon

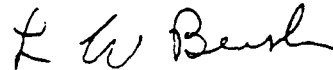
J. W. Salmon, Manager
Engineering Analysis Department
Research, Test, & Engineering

ENCLOSURE (1)

DIAMOND TANK
STRESS ANALYSIS

6 MARCH 1989

PREPARED BY:



L. W. Bush
Structural Analysis Section
Engineering Analysis Department

APPROVED BY:

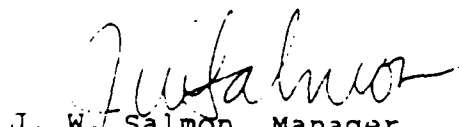


J. E. Jellison, Manager
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REVIEWED BY:



R. K. Ishikawa
Structural Analysis Section
Engineering Analysis Department



J. W. Salmon, Manager
Engineering Analysis Department
Research, Test & Engineering

STRUCTURAL ANALYSIS REVIEW FORM

DATE: 3-14-89

PROGRAM: Diamond Tank K F J040

COMPONENT: Diamond Tank

PURPOSE of ANALYSIS: Perform stress analysis to determine feasibility of the diamond tank for a proposal to AFAL.

ANALYSIS PROGRAM & VERSION:
TAPE SAVE SET & FILE NAMES:

Saved by archive under

E24118-Diamond

MATERIALS: (Material Name)	VALUE OR PAGE NUMBER	INFORMATION SOURCE	APPROVAL
1. Diamond	6,7	Deena Morgan	DBM
2. ~~2~~ Beryllium	10	A	

LOADS & TEMPERATURE:

1. PRESSURE
 - a. Steady State
 - b. Transient
2. TEMPERATURE DISTRIBUTION
 - a. Steady State
 - b. Transient
3. THRUST AND THRUST TRANSIENT
4. ACCELERATION
5. VIBRATION
6. ACOUSTIC
7. LOAD HISTORY

25,000 psi Deena Morgan DBM

GEOMETRY AND PHYSICAL CHARACTERISTICS:

1. Dimensions
2. Boundary Conditions
3. Weights and Masses
4. Stiffness

10.0 dia, .023 wall Deena Morgan DBM

INFORMATION SOURCE LEGEND:

- A. Mil Hdbk 5
- B. Rep. MA-81-107
- C. Specs 1. _____
2. _____ 3. _____
- D. Drawings 1. _____
2. _____ 3. _____
- E. Reports 1. _____
2. _____ 3. _____

- F. Verbal _____
- G. Estimate _____
- H. Calculated _____
- I. Layout _____
- J. Lab Tests _____
- K. _____
- L. _____
- M. _____

I. INTRODUCTION

Recently it has become possible to make thin films of diamond. Assuming it becomes possible to make films of reasonable thickness the obvious question is can the tremendous strength of diamond be used in structural applications. This analysis examines using diamond to make pressure vessels. The goal of such a tank would be a very high pressure tank and very light weight.

A spherical tank design was chosen since this is the most efficient shape for a pressure vessel made from a uniform strength shell material. The real challenge of such a design is to minimize the stress concentration effect of the filler neck. This analysis hence focused on that region.

Four Finite Element models were made to investigate various shapes of the transition from the spherical tank to the filler neck. The first model had the liner material cover the entire inner surface of the tank. This showed that, if that is the case, the liner would yield.

The second model removed the liner from all areas except the neck. The neck/tank transition was a 1.0 in radius fillet. The third model used a parabola to make the transition. The fourth model locally thickened areas of high stress.

The actual size and pressure of the tank analyzed is not important. What is significant is the stress concentration factor achieved. With it any size and pressure tank can be designed and its weight predicted.

Summary of Results:

Stress Concentration Factors

	<u>Concentration Factor</u>
Model #2	2.32
Model #3	1.51
Model #4	1.25

Discussion:

- Model #2 is a 1.0" radius fillet
- Model #3 is a parabola fillet
- Model #4 is model #3 with local thickening

Conclusions:

The best stress concentration factor achieved for a uniform thickness tank is 1.51; for any tank the best configuration analyzed it is 1.25. Similar results are expected for any tank size and pressure using the following formula.

$$\text{Stress} = (\text{Concentration Factor}) \frac{a^3 + 2b^3}{a^3 - b^3} \frac{\text{pressure}}{2}$$

Where a = Outside Radius

b = Inside Radius

Recommendation

Use the following for design

$$\frac{PD}{4t} \cdot (\text{Concentration Factor}) = \sigma \text{ stress}$$

Check final design using thick sphere formula of the conclusions.

ANALYSIS

Design Criteria

1.5 on ultimate

1.0 on yield

Load and Environment

As a design point use 25000 psi internal pressure, 70°F. Note model #1 was run with 20,000 psi.

Material Properties

The following few pages detail the material properties received and the manipulation of them to a form acceptable for the finite element model.

Material property conversions use equation of Mechanics of Composite Materials: 1975 Jones.

$$\frac{\text{dyne}}{\text{cm}^2} \cdot 1.450 \times 10^{-5} = \text{psi}$$

$$\frac{\text{dyne}}{\text{cm}^2} \cdot 2.248 \times 10^{-6} \frac{\text{Lb}}{\text{dyne}} \cdot (2.54)^2 \frac{\text{cm}^2}{\text{in}^2}$$

$$\begin{array}{ll} C_{11} & 11 \\ C_{12} & 12 \\ C_{44} & 44 \end{array} \quad \text{Assume } C_{11} = C_{22} = C_{33}$$

$$\begin{array}{llll} C & = & 3.66034 & \text{E-24} & 19 \\ S_{11} & = & 6.56337 & \text{E-9} & 21 \\ E_1 & = & 1.5236 & \text{E-8} & 20 \\ S_{12} & = & -6.733 & \text{E-10} & 22 \\ S_{44} & = & 1.20569 & \text{E-8} & 23 \\ \sqrt{12} & = & .102585 & & 24 \\ G_{12} & = & 8.294 & \text{E-7} & 25 \end{array}$$

Data:

$$\text{Compressibility: } \frac{\text{cm}^2}{\text{dyne}} = 2.3 \times 10^{-13}$$

$$\text{Compressive Strength} = 9.65 \times 10^{11} \frac{\text{dynes}}{\text{cm}^2}$$

$$C_{11} = 107.6 \times 10^{11} \frac{\text{dynes}}{\text{cm}^2}$$

$$C_{12} = 12.3 \times 10^{11} \frac{\text{dynes}}{\text{cm}^2}$$

$$C_{44} = 57.2 \times 10^{11} \frac{\text{dynes}}{\text{cm}^2}$$

$$\text{Shear Strength} = ?$$

E: Youngs Modulus = 10.35×10^{12} dynes/cm²

C₁₁ = 1.5602 E8 psi

C₁₂ = 1.7835 E7 psi

C₄₄ = 8.294 E7 psi

E = 1.50 E8 psi

Tensile Strength = 3.00×10^6 psi (Synthetic)

GEOMETRY AND PHYSICAL CHARACTERISTICS

Model #1

10" Dia

.023" Shell

.05" Liner

1.0" Radius Fillet to

1/4" OD Line .05" hole

.1" Wall (Line)

$q = 20,000$ psi internal pressure

$$\sigma = \frac{q}{2} \frac{a^3 + 2b^3}{a^3 - b^3} = 2.17 \text{ MSI}$$

Model #2

Same as model #1 except liner is only in the neck regions.

Model #3

Same as Model #2 except 1/2 of the 1.0" fillet radius replaced by a parabola which matches slope at 45° point of fillet.

Model #4

Same as Model #3 except some local thickening of sphere where max stress occurs near the neck. 37% max thickness increase.

METHOD OF ANALYSIS

A finite element analysis of the tank and neck are used together with hand calculations to determine the stress concentration factor for that particular geometry.

The ANSYS finite element code is the program used. Only elastic analyses were performed.

Hand analysis used the following:

Thick Sphere Equation

$$\sigma = \frac{P}{2} \cdot \frac{a^3 + 2b^3}{a^3 - b^3}$$

Where

a = Outer Radius

b = Inner Radius

DETAILED ANALYSIS

Model #1

10.0 in dia

0.023 diamond wall

0.050 Beryllium liner

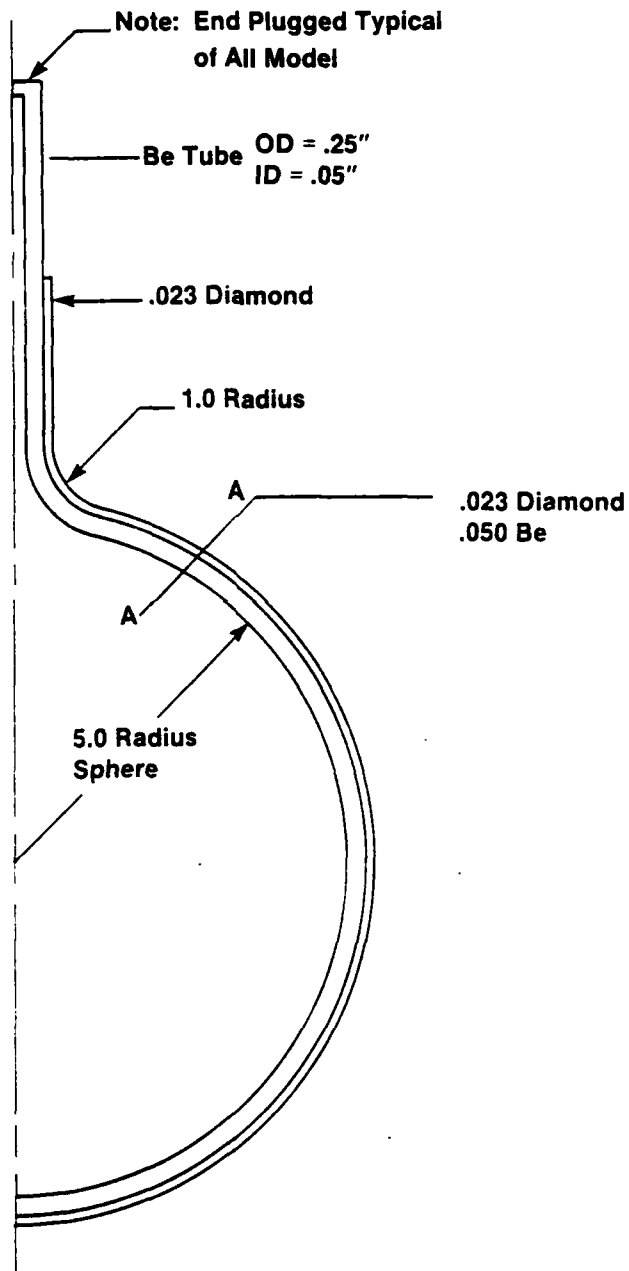
Model #1 Results

The Beryllium of the shell carried an excessive amount of stress. If a plastic analysis had been run it would have yielded substantially. Because of the incorrect load sharing the stress results are not usable.

Model #2

Similar to Model #1 except the beryllium is only in the neck. Pressure is 25,000 psi.

Fillet Details

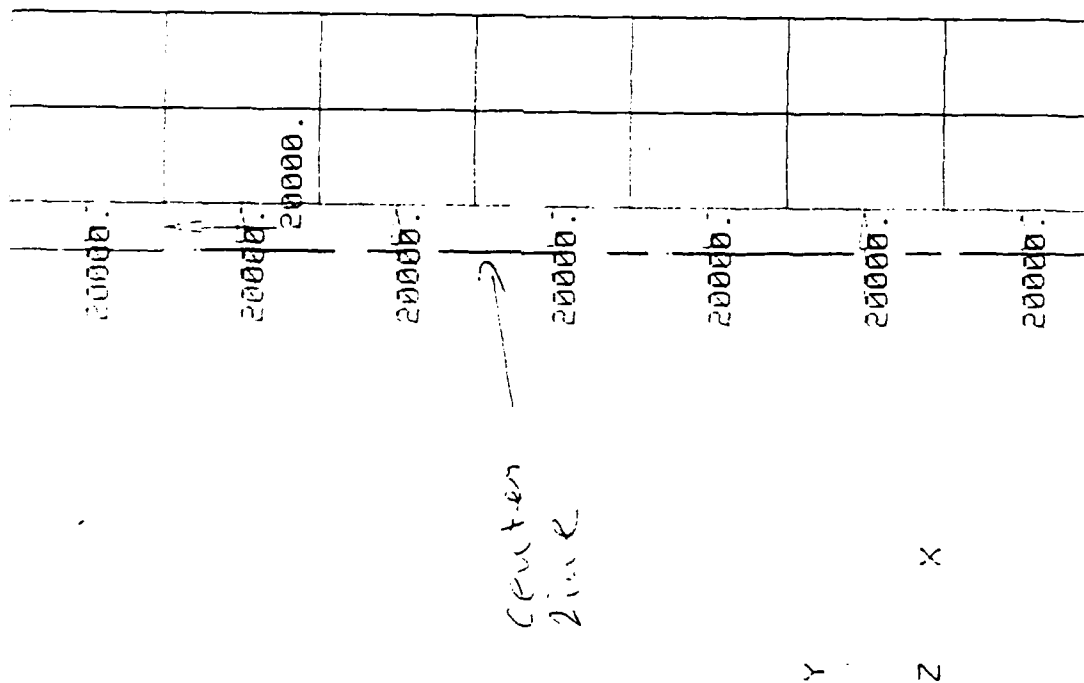


Material Data as Used by F.E. Models

LIST ALL MATERIALS PROPERTY= ALL

PROPERTY TABLE DENS	MAT= 1	NUM. POINTS= 2	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.32900E-03	70.000	0.32900E-03
PROPERTY TABLE EX	MAT= 1	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.15200E+09		
PROPERTY TABLE NUXY	MAT= 1	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.10300		
PROPERTY TABLE ALPX	MAT= 1	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.63000E-05		
PROPERTY TABLE GXY	MAT= 1	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.847269E8		
PROPERTY TABLE DENS	MAT= 2	NUM. POINTS= 2	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.17100E-03	70.000	0.17100E-03
PROPERTY TABLE EX	MAT= 2	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.42000E+08		
PROPERTY TABLE NUXY	MAT= 2	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.10000		
PROPERTY TABLE ALPX	MAT= 2	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	0.62000E-05		
PROPERTY TABLE GXY	MAT= 2	NUM. POINTS= 1	
TEMPERATURE DATA		TEMPERATURE DATA	
70.000	2.3333E7		

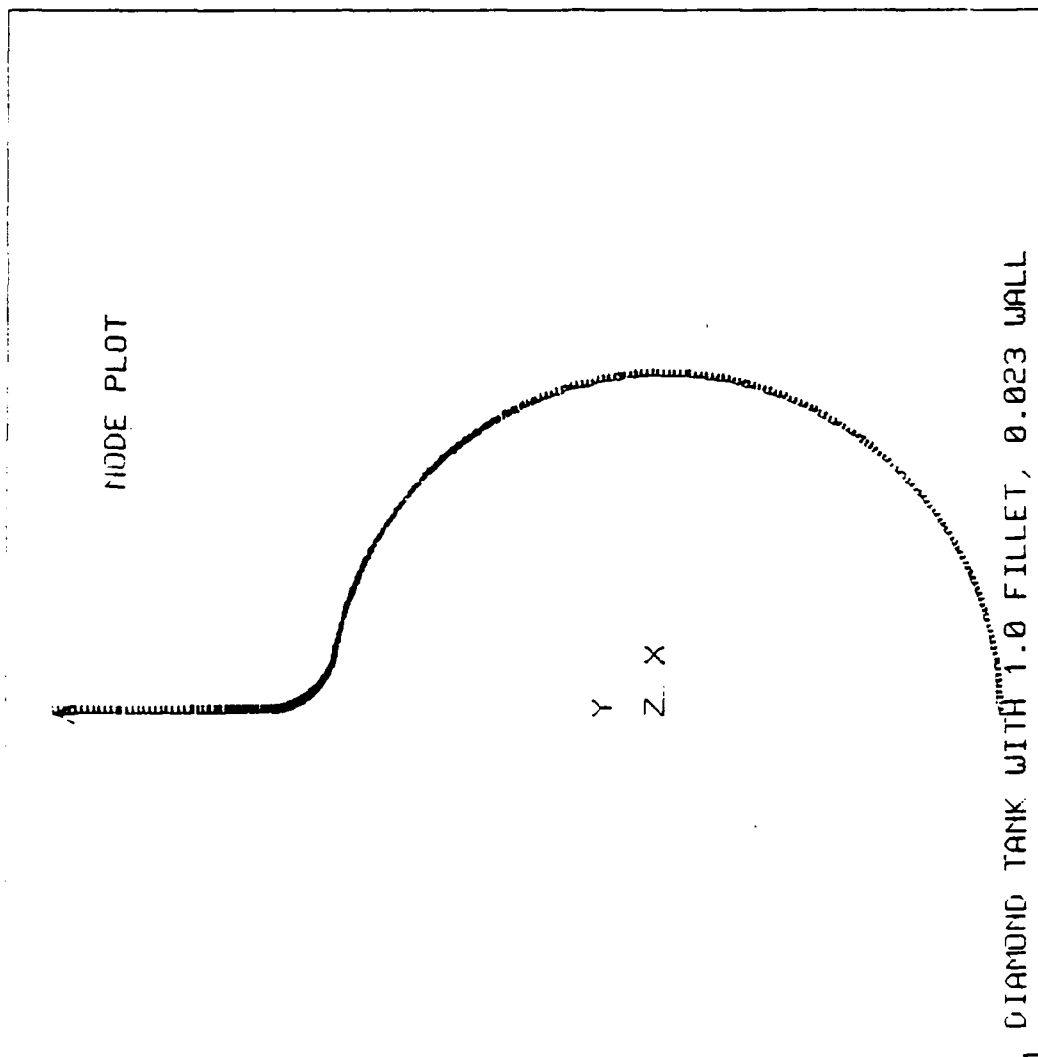
Beryllium
Source
M11-5



MODEL 1. GEOMETRY 2. ANALYSIS MODEL 3. ANALYZE 4. RESULTS 5. INTERFACE 6. STOP
MODEL DETAIL AT END OF FILLER TUBE SHOWING PLUGGED END.

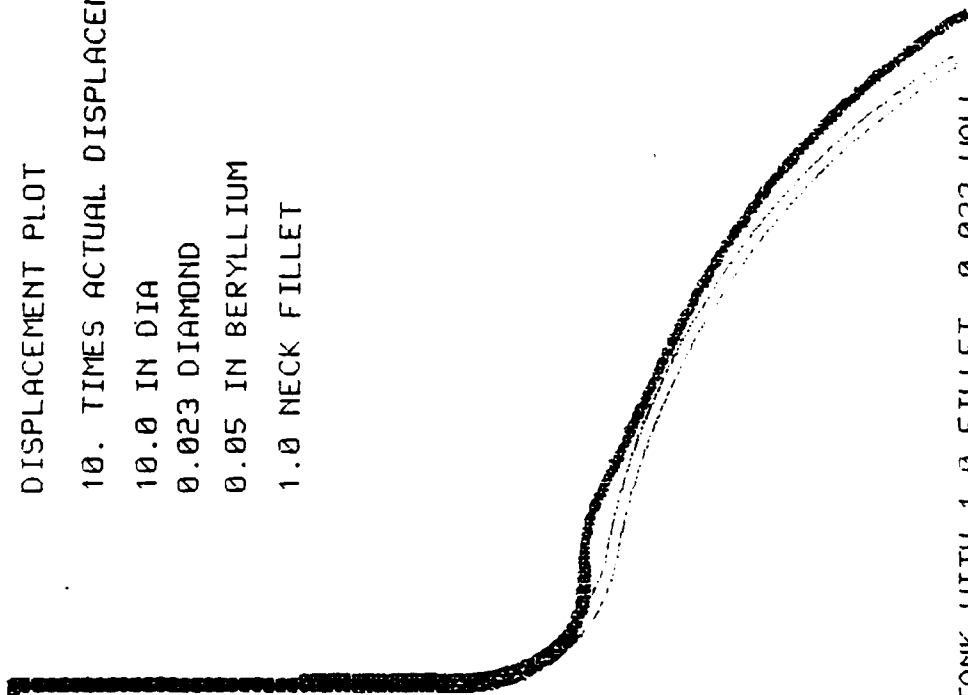
ANSYS 4.3
MAR 6 1989
13:57:39
PREP7 NODES
TDIS BC
PRES BC

ZU=1
DIST=7.7
XF=2.5
YF=2
MX=20000
MY=20000
NCON=18
UMIN=20000



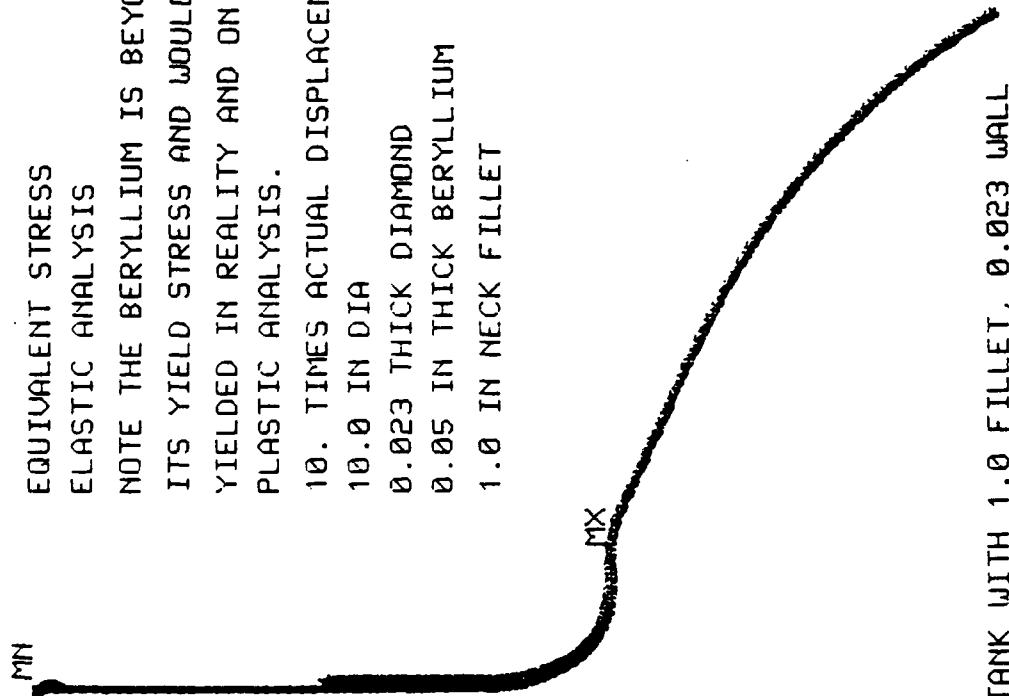
ANSYS 4.3
 MAR 2 1989
 8:28:17
 POST1 DISPL.
 STEP=1
 ITER=1
 ZV=1
 DIST=3.57
 XF=2.15
 YF=5.76
 DMAX=.035
 * DSCA=10

DISPLACEMENT PLOT
 10. TIMES ACTUAL DISPLACEMENT
 10.0 IN DIA
 0.023 DIAMOND
 0.05 IN BERYLLIUM
 1.0 NECK FILLET



DIAMOND TANK WITH 1.0 FILLET, 0.023 WALL

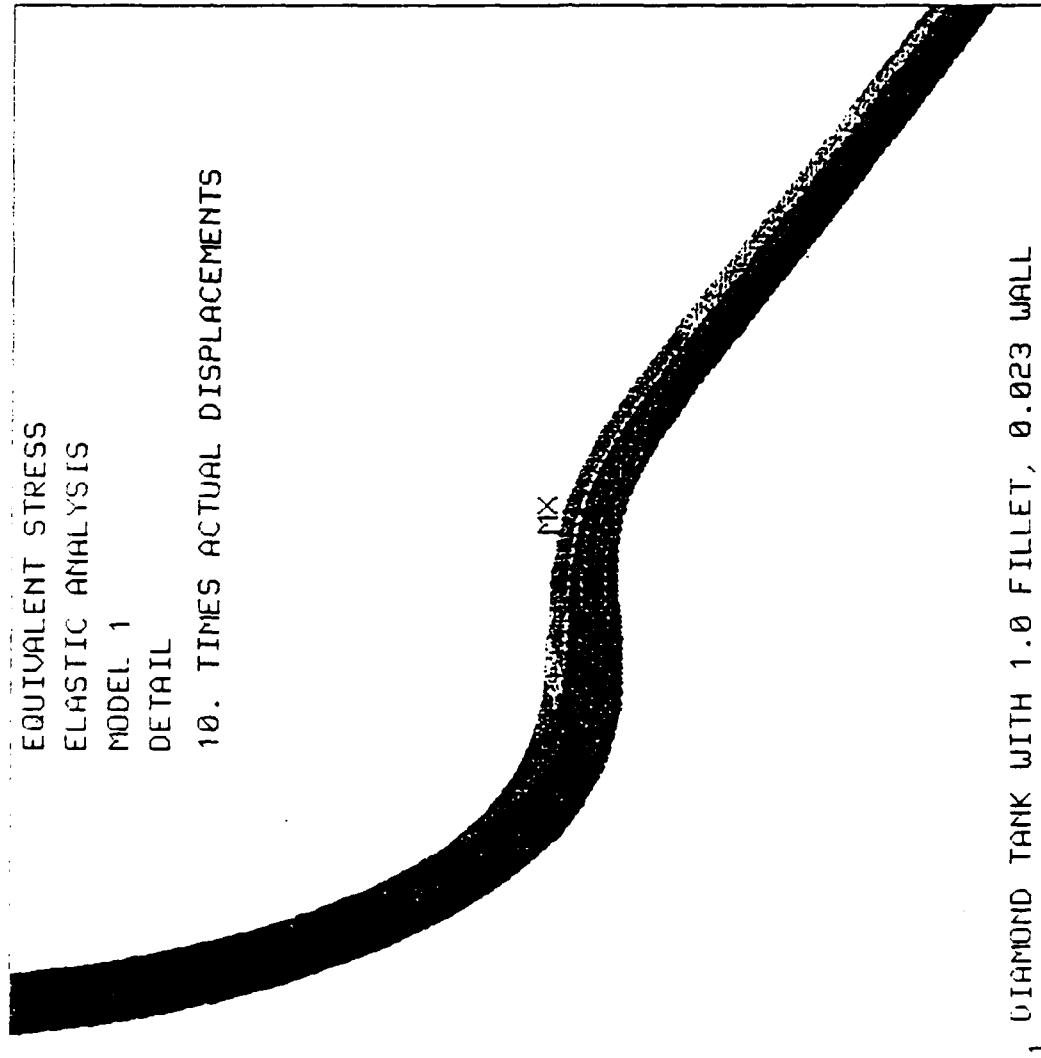
EQUIVALENT STRESS
 ELASTIC ANALYSIS
 NOTE THE BERYLLIUM IS BEYOND
 ITS YIELD STRESS AND WOULD HAVE
 YIELDED IN REALITY AND ON A
 PLASTIC ANALYSIS.
 10. TIMES ACTUAL DISPLACEMENTS.
 10.0 IN DIA
 0.023 THICK DIAMOND
 0.05 IN THICK BERYLLIUM
 1.0 IN NECK FILLET



1 DIAMOND TANK WITH 1.0 FILLET, 0.023 WALL

ANSYS 4.3
 MAR 2 1989
 8:49:55
 POST1 STRESS
 STEP=1
 ITER=1
 SIGE (AUG)
 ZU=1
 DIST=3.57
 XF=2.15
 YF=5.76
 MX=1968247
 MN=567
 219195
 437827
 656459
 875091
 1093723
 1312355
 1530987
 1749619
 1968247

EQUIVALENT STRESS
 ELASTIC ANALYSIS
 MODEL 1
 DETAIL
 10. TIMES ACTUAL DISPLACEMENTS



1 DIAMOND TANK WITH 1.0 FILLET, 0.023 WALL

ANSYS 4.3
 MAR 2 1989
 8:49:55
 POST1 STRESS
 STEP=1
 ITER=1
 SIGE (AUG)

ZOOM
 ZU=1
 * DIST=1.05
 * XF=1.02
 * YF=5.12
 YRTO=1.7
 MX=1968247
 MN=567
 219195
 437827
 656459
 875091
 1093723
 1312355
 1530987
 1749619
 1968247

$$\sigma = 2.7174 \text{ MSI}$$

Stress Concentration Factor

$$\text{C. F.} = \frac{\sigma_{\max}}{\sigma} = 2.335$$

Model #3

Similar to Model #2 except fillet modified to a parabola shape. The following two pages are my scratch calculations that defined the parabola's shape. The $A_x \dots D_z$ coef's were input by the Patran programs Line-Algebraic command. Coef's not defined are zero. The coef's are defined to match slope and position at the two points:

$$(.541252, 5.0942) \quad \text{and} \quad (1.44167, 4.78765)$$

The uniform thickness of the shell was maintained over this region.

$$A_z B_z C_z D_z = 0$$

$$X(\xi) = A_x \xi^3 + B_x \xi^2 + C_x \xi + D_x$$

$$Y(\xi) = A_y \xi^3 + B_y \xi^2 + C_{xy} \xi + D_x$$

$$\text{Intersect } M \Rightarrow \xi = 0, N = \xi = 1$$

$$x@M = 1.44167 + D_x$$

$$x@N = .541252 = A_x + B_x + C_x + D_x$$

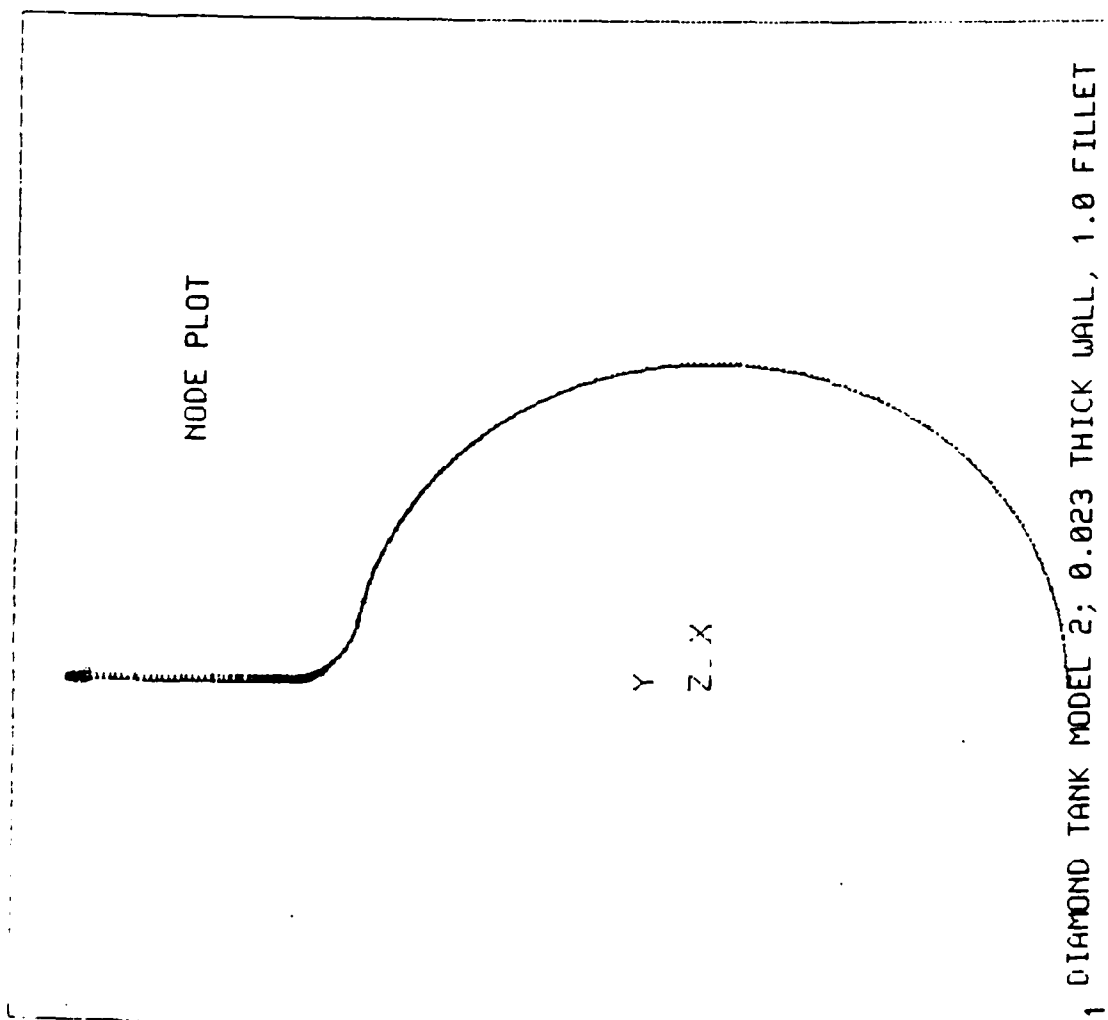
$$y@M = 4.78765 = +D_y$$

$$y@N = 5.09426 = A_y + B_y + C_y + D_y$$

Slope at M

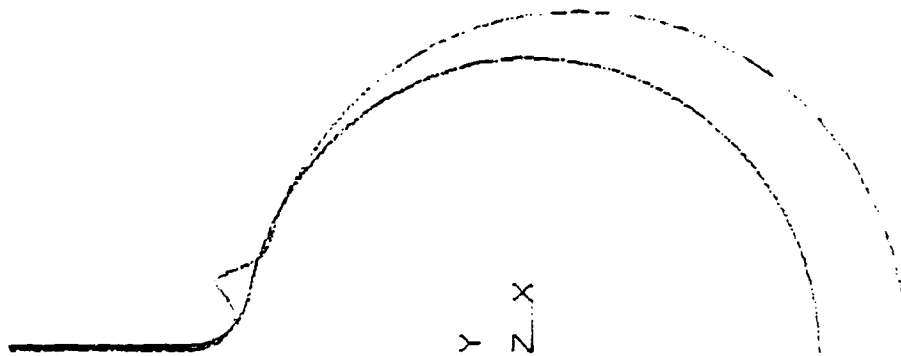
$$\text{Slope @ M} = \frac{(SM)}{-.30111882} = \frac{dy}{dx} = \frac{3A_y \xi^2 + 2B_y \xi + C_y}{3A_x \xi^2 + 2B_x \xi + C_x}$$

ANSYS 4.3
 MAR 2 1989
 15:13:43
 PREP7 NODES
 TDIS BC
 PRES BC
 ZU=1
 DIST=7.7
 XF=2.5
 YF=2
 MX=25000
 MY=25000
 NCON=18
 UMIN=25000



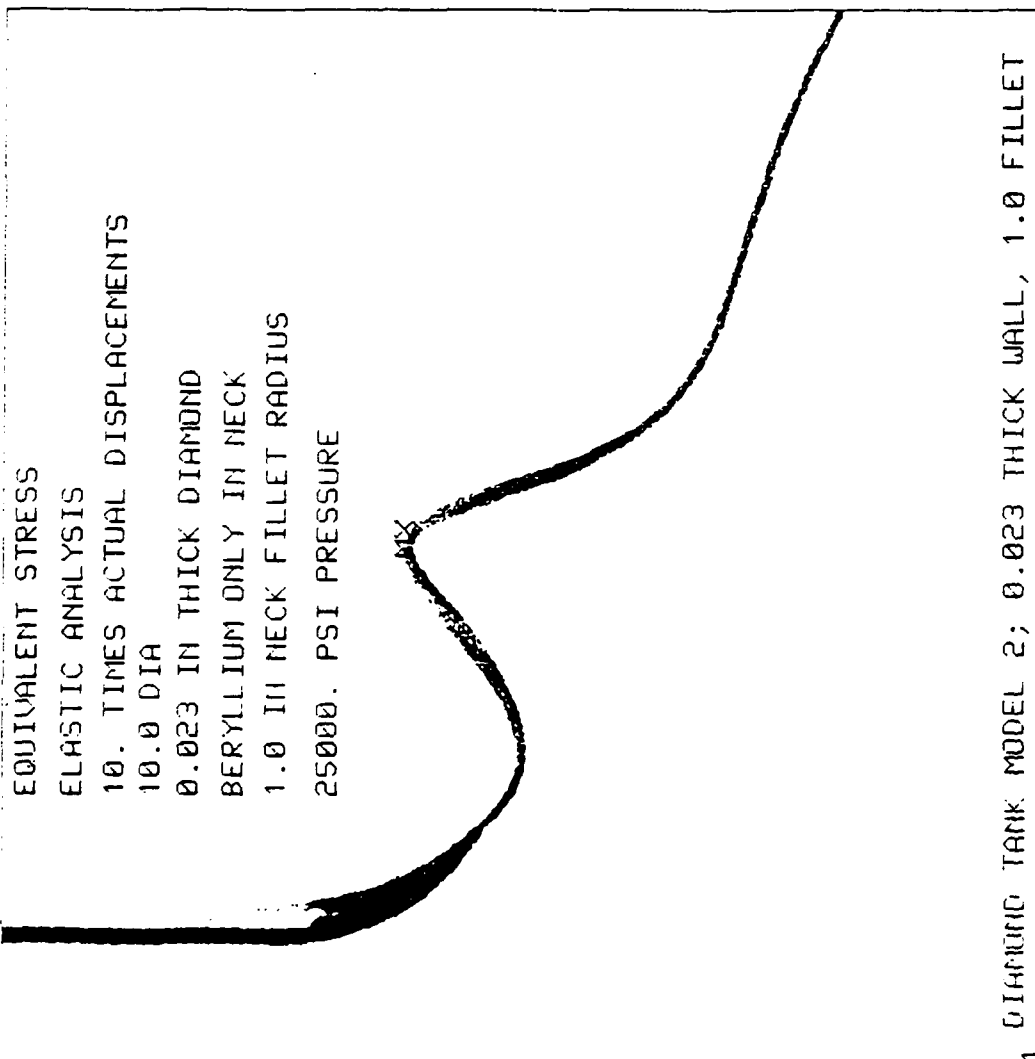
ANSYS 4.3
 MAR 3 1989
 8:33:39
 POST1 DISPL.
 STEP=1
 ITER=1
 ZU=1
 * DIST=9
 * YF=1
 DMAX=.153
 * DSCA=10

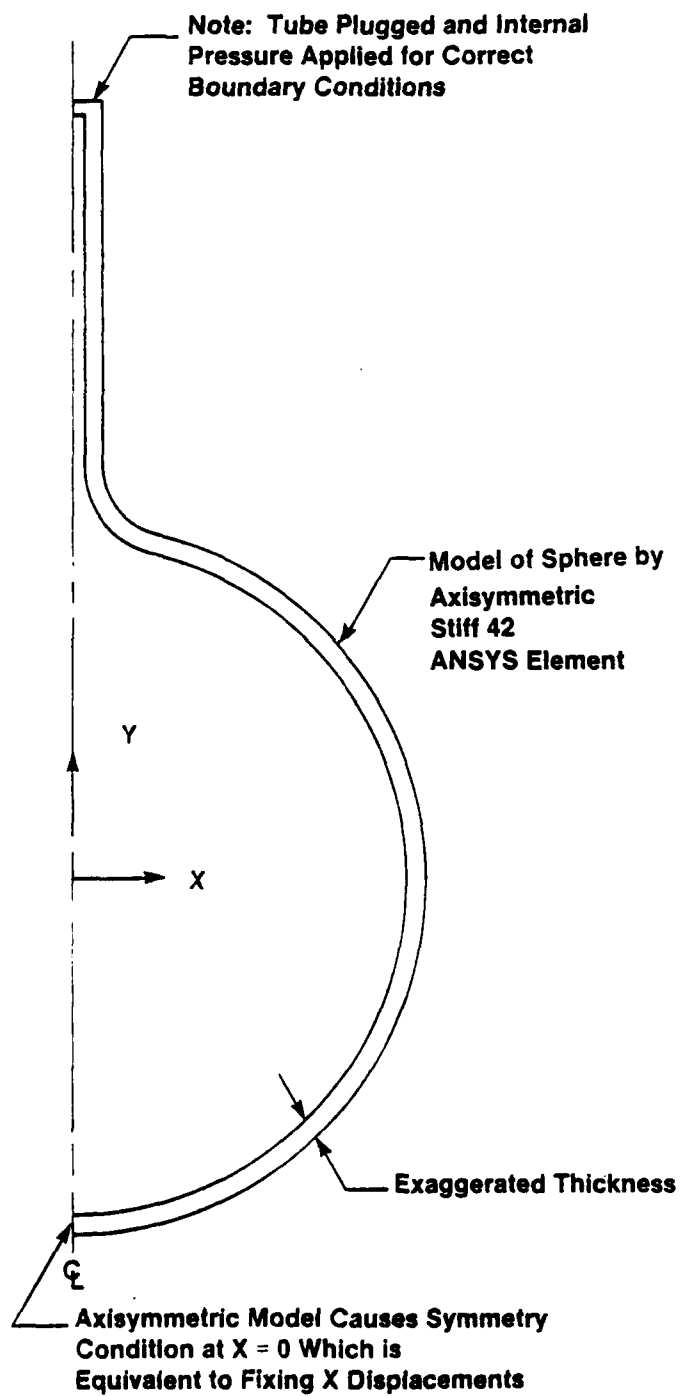
DISPLACEMENT PLOT
 10. TIMES ACTUAL
 DISPLACEMENT
 10.0 IN DIAMETER
 0.023 IN THICK DIAMOND
 BERYLLIUM ONLY IN NECK
 1.0 IN NECK FILLET RADIUS



1 DIAMOND TANK MODEL 2; 0.023 THICK WALL, 1.0 FILLET

ANSYS 4.3
 MAR 3 1989
 9:23:56
 POST1 STRESS
 STEP=1
 ITER=1
 SIGE (AVG)
 ZOOM
 ZU=1
 * DIST=1.57
 * XF=1.22
 * YF=5.12
 MX=6344717
 MN=904
 705769
 1410638
 2115507
 2820376
 3525245
 4230114
 4934983
 5639852
 6344717





Model #2 Results

F. E Model Results

$$\sigma_{\max} = 6.345 \text{ MSI}$$

Hand Calcs

$$\sigma = \frac{P}{2} \cdot \frac{a^3 + 2b^3}{a^3 - b^3}$$

$$a = 5.000 \text{ in}$$

$$b = 5.023 \text{ in}$$

$$\sigma = 2.7174 \text{ MSI}$$

Stress Concentration Factor

$$\text{C. F.} = \frac{\sigma_{\max}}{\sigma} = 2.335$$

Model #3

Similar to Model #2 except fillet modified to a parabola shape. The following two pages are my scratch calculations that defined the parabola's shape. The $A_x \dots D_z$ coef's were input by the Patran programs Line-Algebraic command. Coef's not defined are zero. The coef's are defined to match slope and position at the two points:

$$(.541252, 5.0942) \quad \text{and} \quad (1.44167, 4.78765)$$

The uniform thickness of the shell was maintained over this region.

$$A_z B_z C_z D_z = 0$$

$$X(\xi) = A_x \xi^3 + B_x \xi^2 + C_x \xi + D_x$$

$$Y(\xi) = A_y \xi^3 + B_y \xi^2 + C_{xy} \xi + D_x$$

$$\text{Intersect } M \Rightarrow \xi = 0, N = \xi = 1$$

$$x@M = 1.44167 + D_x$$

$$x@N = .541252 = A_x + B_x + C_x + D_x$$

$$y@M = 4.78765 = +D_y$$

$$y@N = 5.09426 = A_y + B_y + C_y + D_y$$

Slope at M

$$\text{Slope @ M} = \frac{(SM)}{-.30111882} = \frac{dy}{dx} = \frac{3A_y \xi^2 + 2B_y \xi + C_y}{3A_x \xi^2 + 2B_x \xi + C_x}$$

$$\text{Slope @ M } \xi = 0 \quad SM = \frac{C_y}{C_x}$$

Slope @ N $\xi = 1$

$$\frac{(SN)}{-.76332478} = \frac{3A_y + 2B_y + C_y}{3A_x + 2B_x + C_x}$$

0 =

$$.41617857 = 1.0644436 B_x + 2 (.03547719 - .30111882 B_x)$$

$$.34522419 = .46220596 B_x$$

$$B_x = .74690554 \quad 04$$

$$B_y = -.1894301 \quad 05$$

$$C_x = -1.6473236 \quad 06$$

$$C_y = .49604012 \quad 07$$

$$D_x = 1.44167 \quad 08$$

$$D_y = 4.78765 \quad 09$$

$$Li, 100, AL, 0/.74690554/$$

Model #3 Results

F. E Results

$$\sigma_{max} = 4.109 \text{ MSI}$$

Hand Calcs

$$\text{Same as before } \sigma = 2.7174 \text{ MSI}$$

Stress Concentration Factor

$$C.F. = \frac{\sigma_{max}}{\sigma} = 1.512$$

Model #4

Similar to Model #3 except the region which in Model #3 has the maximum stress the thickness is increased 37%.

37% was selected by the following method:

$$\text{Stress (\#3)} = \text{Shell} + \text{bending}$$

$$4.109 = 2.7174 + \text{bending}$$

$$1.379 = \text{bending}$$

Now increase thickness to produce zero concentration.

$$2.73 = 2.73 \left(\frac{1}{t} \right) + 1.379 \left(\frac{1}{t^2} \right)$$

$$\text{Let } x = \frac{1}{t}$$

$$(1.379) x^2 + 2.73 x - 2.73 = 0$$

$$x = .7304$$

$$t = 1.37$$

This increased thickness was blended into the nominal. The max thickness is at point of max stress of Model #3.

Model #4 Results

F.E Results

$$\sigma_{\max} = 3.400 \text{ MSI}$$

Hand Calcs

Same as before

$$\sigma = 2.7174 \text{ MSI}$$

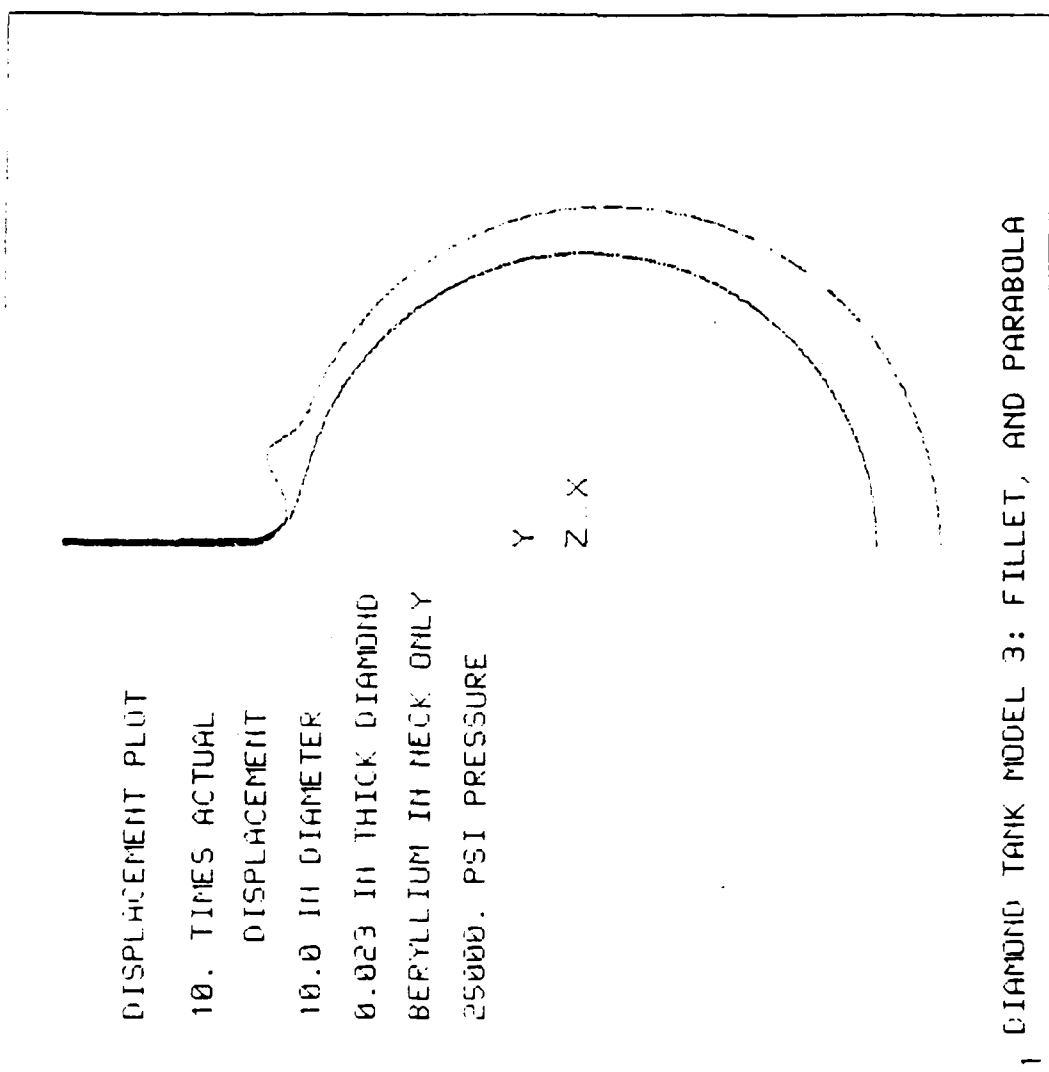
Stress Concentration Factor

$$\text{C. F.} = \frac{3.40}{2.7174} = 1.251$$

Note if the exact geometry of Model #4 is desired it will have to be obtained from the Patrayn geometry file.

ANSYS 4.3
 MAR 3 1989
 12:58:41
 POST1 DISPL.
 STEP=1
 ITER=1
 ZU=1
 * DIST=9
 * YF=1
 DMAX=.112
 * DSCA=10

DISPLACEMENT PLOT
 10. TIMES ACTUAL
 DISPLACEMENT
 10.0 IN DIAMETER
 0.023 IN THICK DIAMOND
 BERYLLIUM IN NECK ONLY
 25000. PSI PRESSURE



1 DIAMOND TANK MODEL 3: FILLET, AND PARABOLA

EQUIVALENT STRESS
ELASTIC ANALYSIS

10. TIMES ACTUAL DISPLACEMENT
FOR UPPER PLOT, 1.0 TIMES
DISPLACEMENT FOR LOWER PLOT.

MX

MX

0.023 IN THICK DIAMOND
BERYLLIUM ONLY IN NECK
25000. PSI PRESSURE

1 DIAMOND TANK MODEL 3: FILLET, AND PARABOLA

ANSYS 4.3
MAR 3 1989
13:20:17
POST1 STRESS
STEP=1
ITER=1
SIGE (AUG)

ZU=1
* DIST=1.57
* XF=1.22
* YF=5.12
MX=4109389
MN=904
457400
913899
1370398
1826897
2283396
2739895
3196394
3652893
4109389

POST1 STRESS
STEP=1
ITER=1
SIGE (AUG)

ZU=1
* DIST=1.57
* XF=1.22
* YF=5.12

Check Model #4 for Adequacy @ 20,000 psi

Since the analysis is linear the stresses can be scaled.

$$\sigma = (3.4 \text{ MSI}) \left(\frac{20,000}{25,000} \right) = 2.72 \text{ MSI}$$

$$\begin{aligned} \text{M.S.} &= \frac{\text{Material Ult}}{(\text{Ult S. F.}) \sigma} - 1 \\ &= \frac{3.0 \text{ MSI}}{1.5 \cdot 2.72} - 1 \end{aligned}$$

$$\text{M.S.} = -0.26$$

Determine Max Pressure Allowable for Model #4 Design

Eqm of "Recommendations"		Ult. Stress
↓		↓
$\frac{P \cdot (10.0")}{4 (0.023)}$	(1.251) =	$\frac{3.0}{1.5}$
		↑
		Ult. F. S.

ANSYS 4.3
MAR 3 1989
16:14:48
POST1 DISPL.
STEP=1
ITER=1

ZU=1
* DIST=9
* YF=1
DMAX=.111
* DSCA=10

DISPLACEMENT PLOT
10. TIMES ACTUAL
DISPLACEMENT

10.0 IN DIAMETER

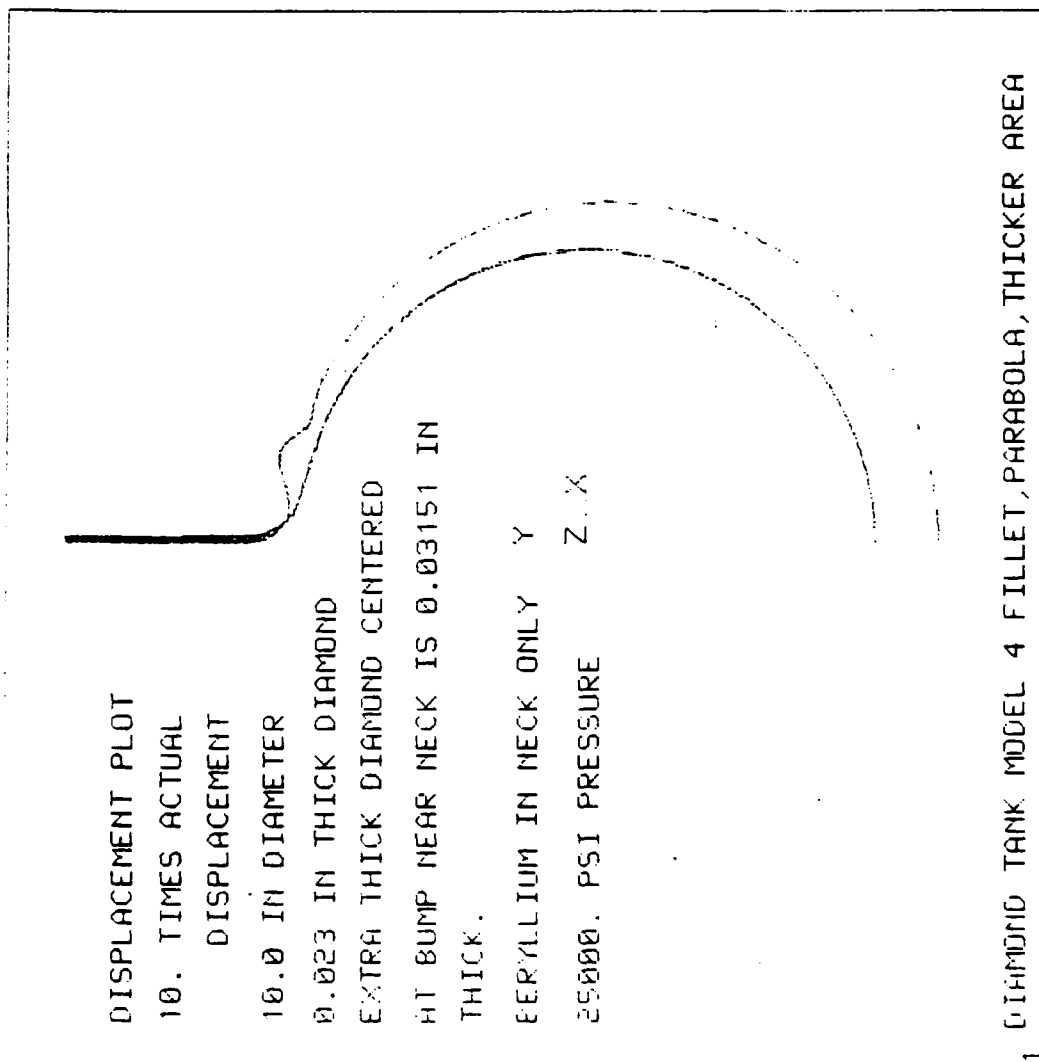
0.023 IN THICK DIAMOND

EXTRA THICK DIAMOND CENTERED

AT BUMP NEAR NECK IS 0.03151 IN
THICK.

BERYLLIUM IN NECK ONLY Y

25000. PSI PRESSURE Z X



1 DIAMOND TANK MODEL 4 FILLET, PARABOLA, THICKER AREA

EQUIVALENT STRESS

ELASTIC ANALYSIS

10. TIMES ACTUAL DISPLACEMENT

FOR UPPER PLOT, 1.0 TIMES

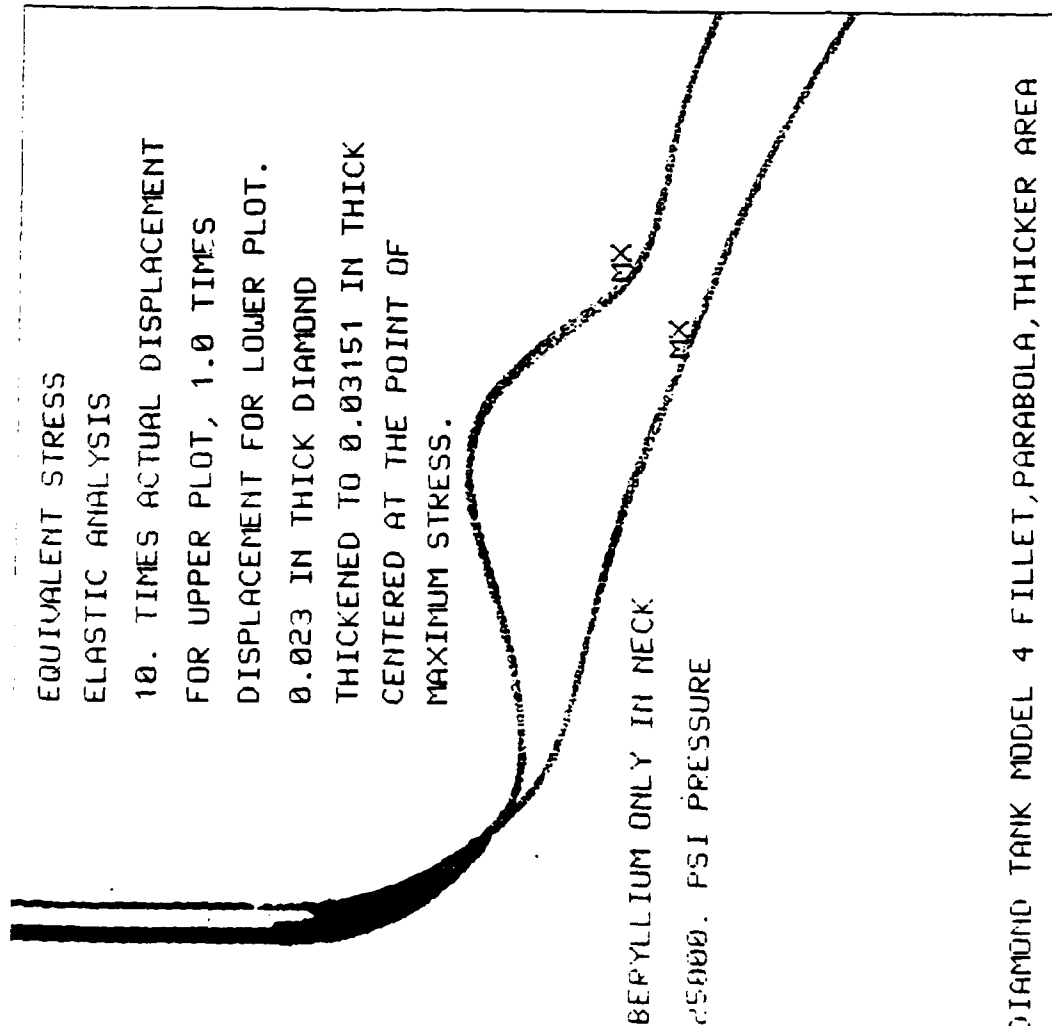
DISPLACEMENT FOR LOWER PLOT.

0.023 IN THICK DIAMOND

THICKENED TO 0.03151 IN THICK

CENTERED AT THE POINT OF

MAXIMUM STRESS.



BERYLLIUM ONLY IN NECK

25000. PSI PRESSURE

1 DIAMOND TANK MODEL 4 FILLET, PARABOLA, THICKER AREA

ANSYS 4.3
MAR 3 1989
16:27:50
POST1 STRESS
STEP=1
ITER=1
SIGE (AUG)

ZU=1

* DIST=1.57

* XF=1.22

* YF=5.12

MX=3400055

MN=904

378585

756269

1133953

1511637

1889321

2267005

2644689

3022373

3400055

POST1 STRESS

STEP=1

ITER=1

SIGE (AUG)

ZU=1

* DIST=1.57

* XF=1.22

* YF=5.12

APPENDIX D

DIFFUSION TEST DATA

APPENDIX D

DIFFUSION TEST DATA INTRODUCTION

The diffusion test raw data consist of a printout of the mass number and concentration of species from mass number 1 (H) to mass number 50 as a function of time. The data presented are for the stability test which used a blank and the four diffusion test windows.

Figure D-1	Stability Test (Blank)	
-2	X	$\theta = 0$ hrs
-3	X	$\theta = 3$ hrs
-4	X	$\theta = 7$ hrs
-5	X	$\theta = 11$ hrs
-6	X	$\theta = 21$ hrs
-7	Specimen 2-Q-31-7	$\theta = 24$ hrs
-8	X	$\theta = 0$ hrs
-9	X	$\theta = 1$ hr
-10	X	$\theta = 1$ hr
-11	Specimen 2-Q-31-8	$\theta = 24$ hrs
-12	X	$\theta = 0$ hrs
-13	X	$\theta = 1$ hr
-14	X	$\theta = 8$ hr
-15	Specimen 2-Q-31-9	$\theta = 24$ hr
-16	X	$\theta = 0$ hr
-17	X	1
-18	X	8
-19	Specimen 2-Q-31-36	24
-20	X	$\theta = 0$ hr
-21	X	1
-22	X	8
		24

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 7/89 9:14

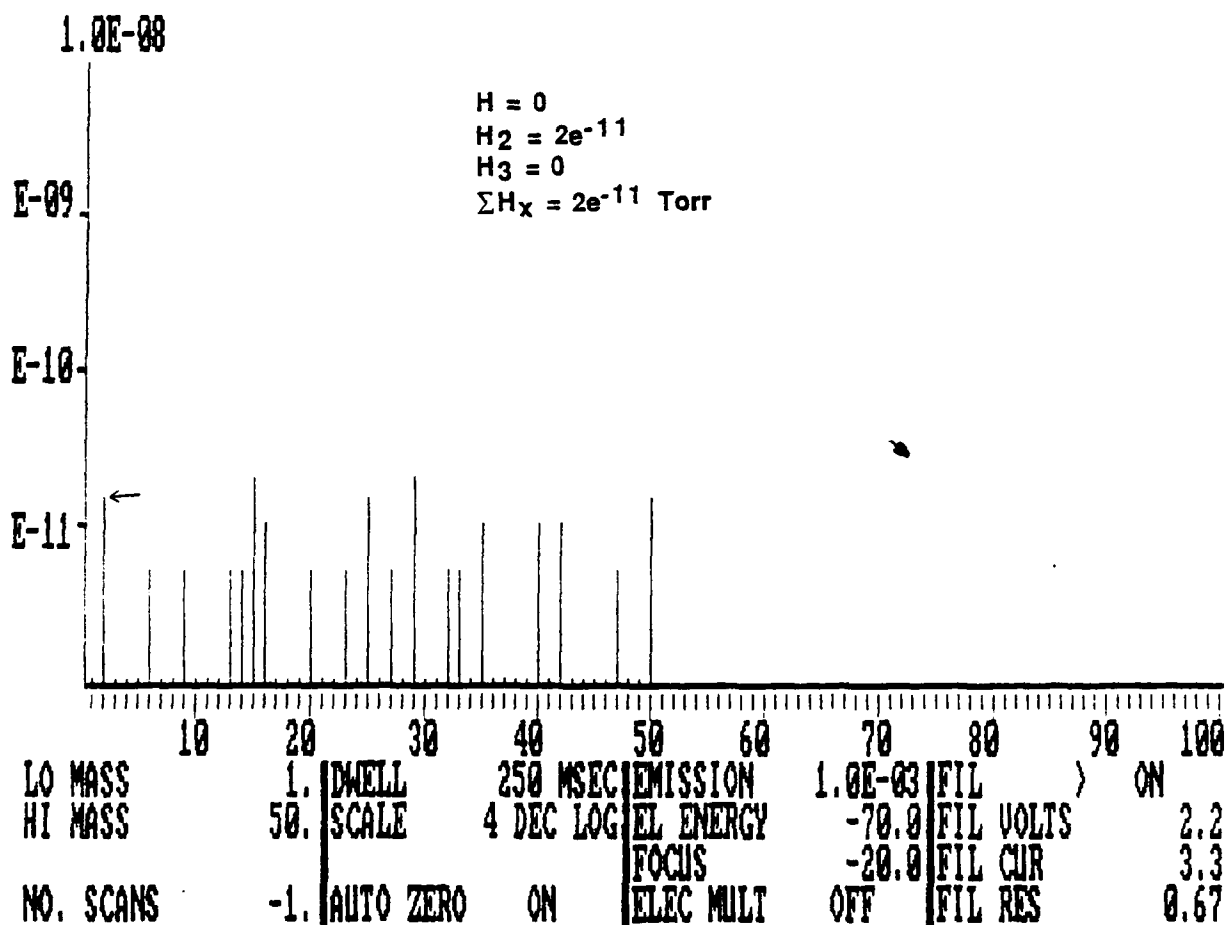


Figure D-1. Stability Test. T = 0 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 7/89 12:19

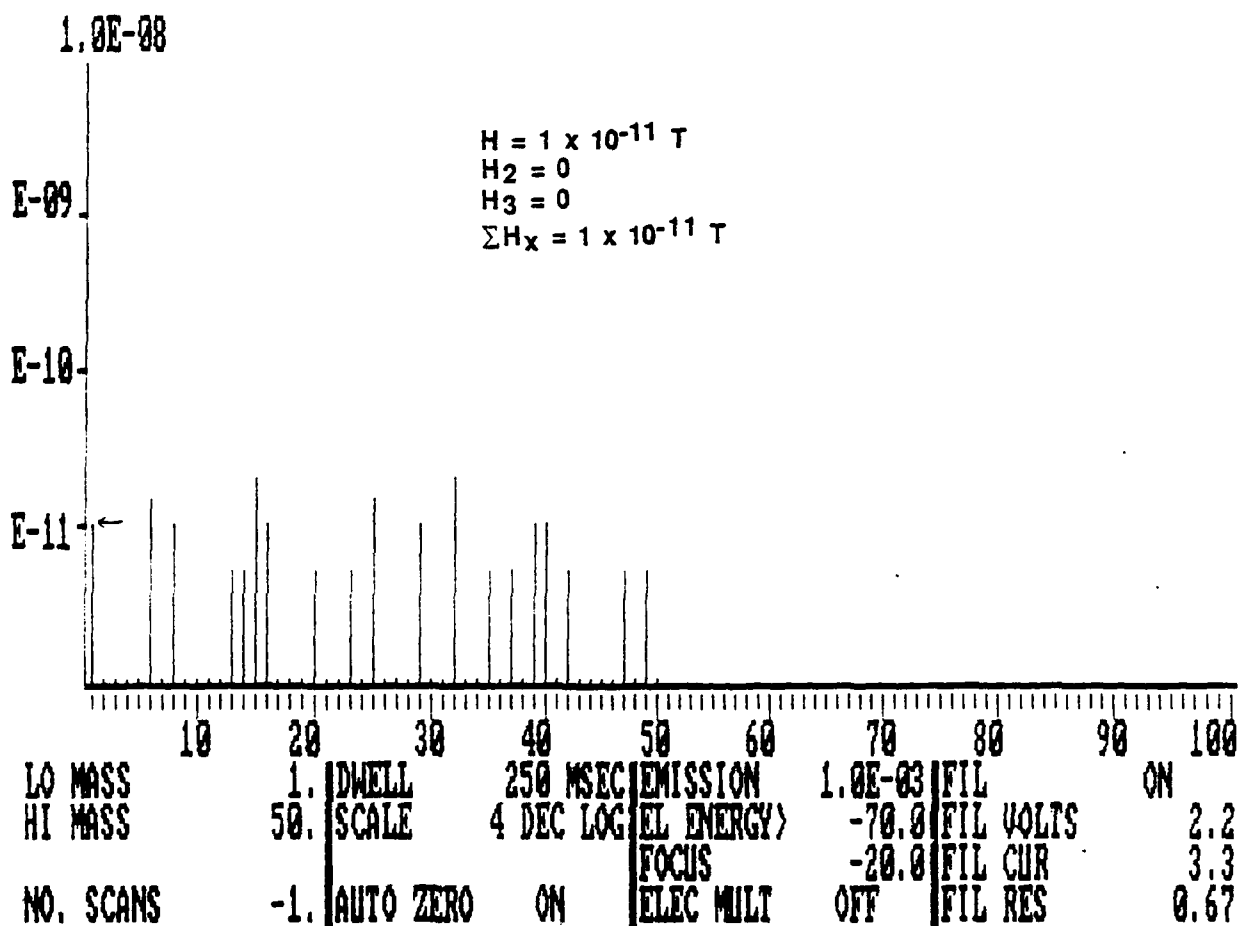


Figure D-2. Stability Test. T = +3 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 7/89 16: 6

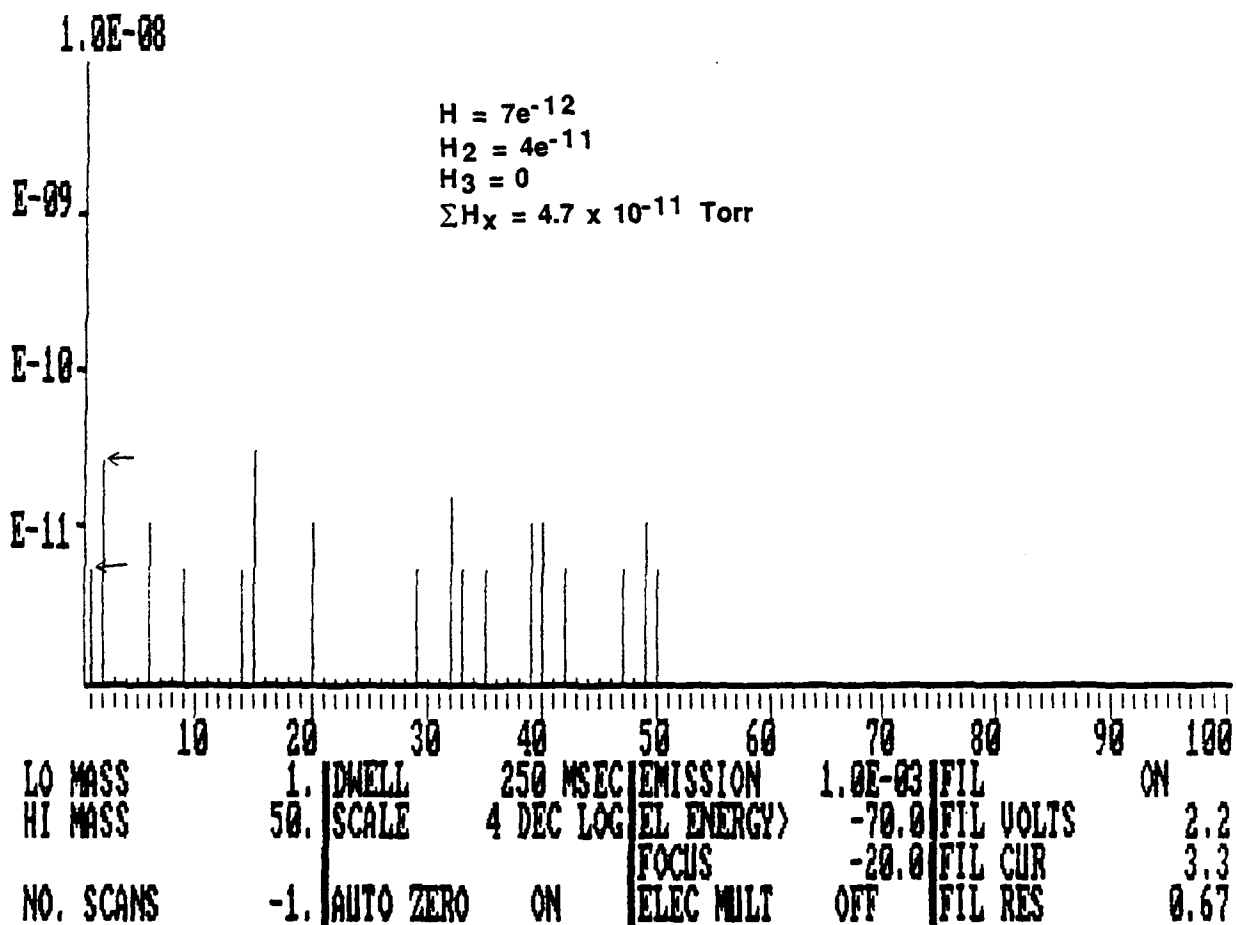


Figure D-3. Stability Test. T = +7 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 7/89 20: 3

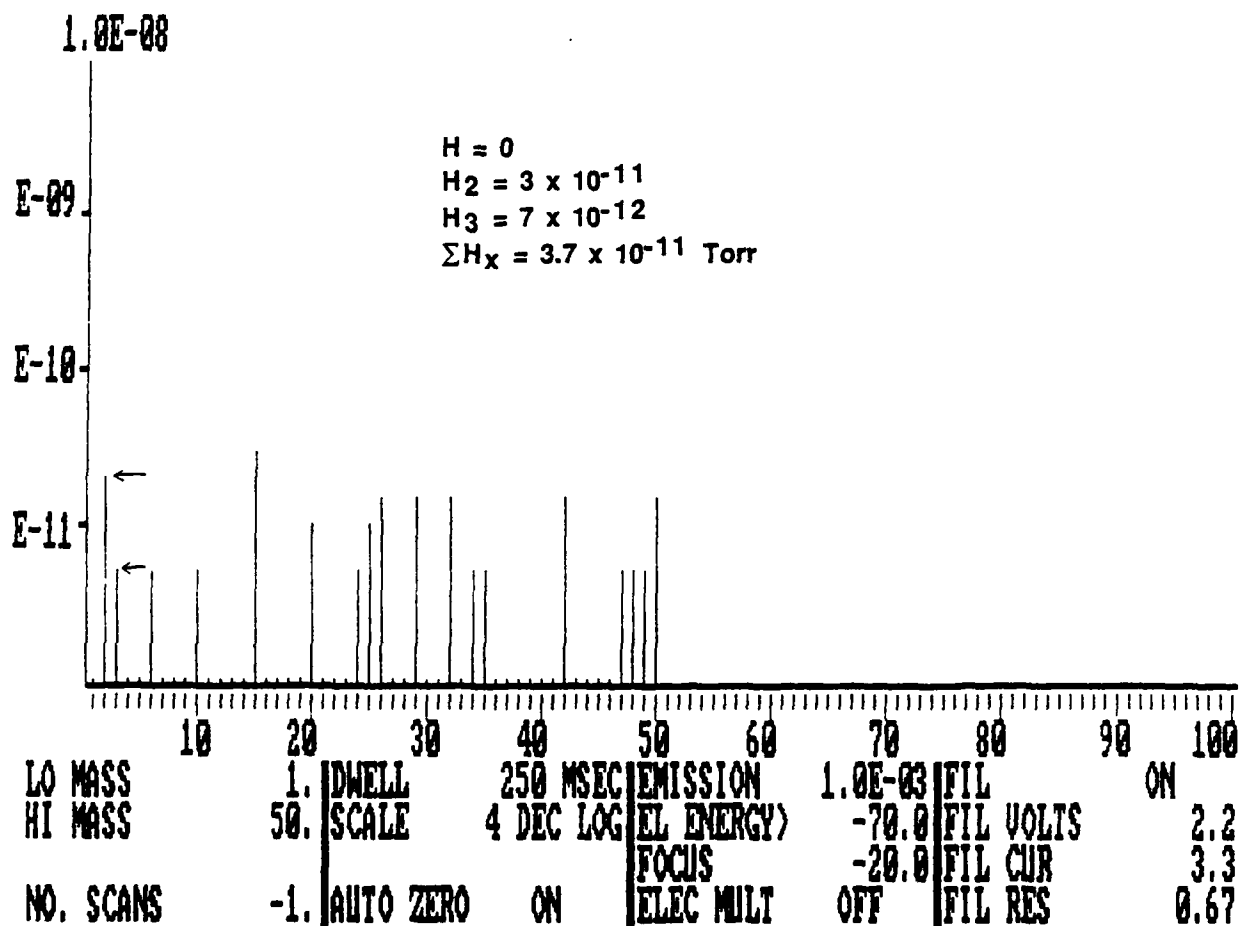


Figure D-4. Stability Test. T = +11 hr.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/ 8/89 6:30

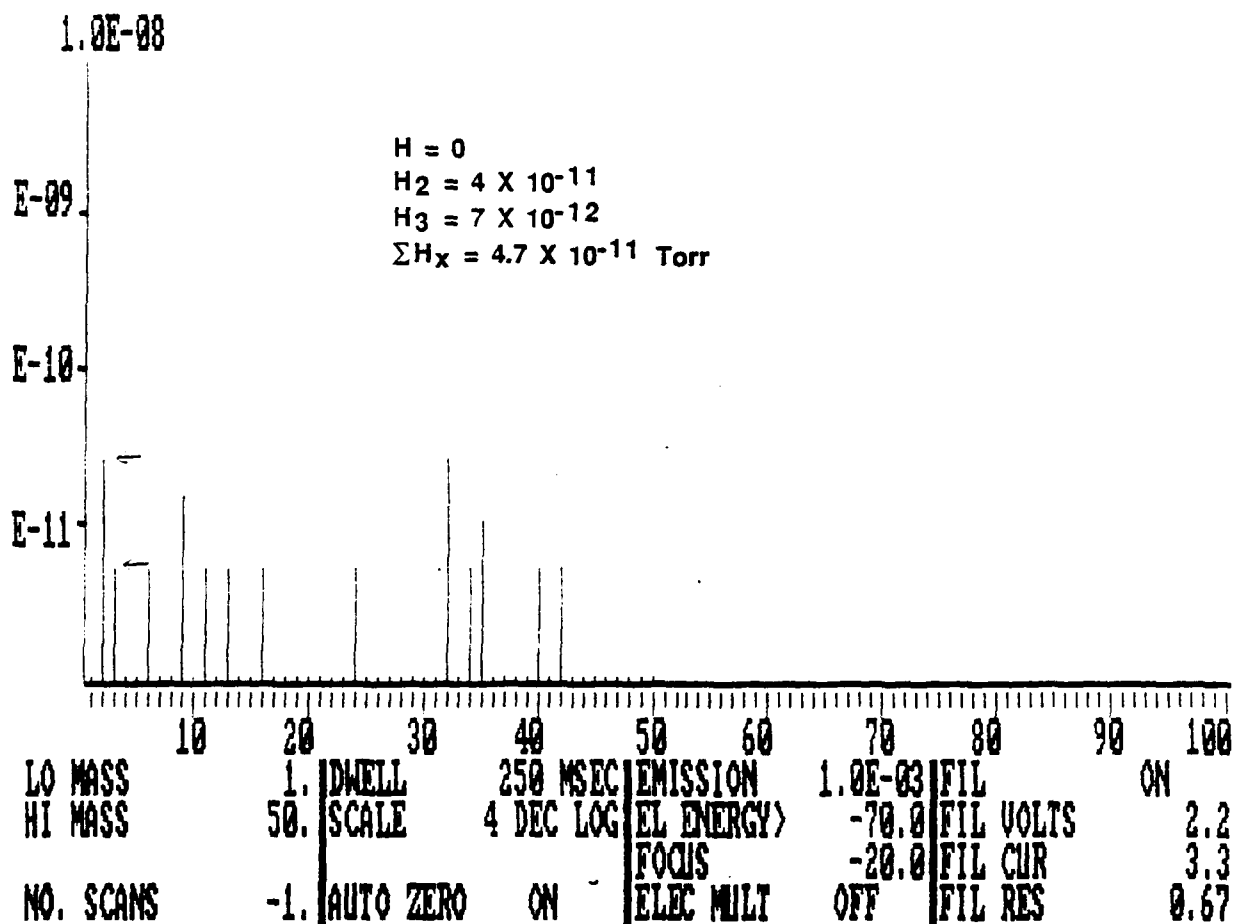


Figure D-5. Stability Test, T = +21 hr.

TOTAL PRS 7.3E-09 DISP SPEC A-B SCAN SPEC A | 2/ 8/89 9:17

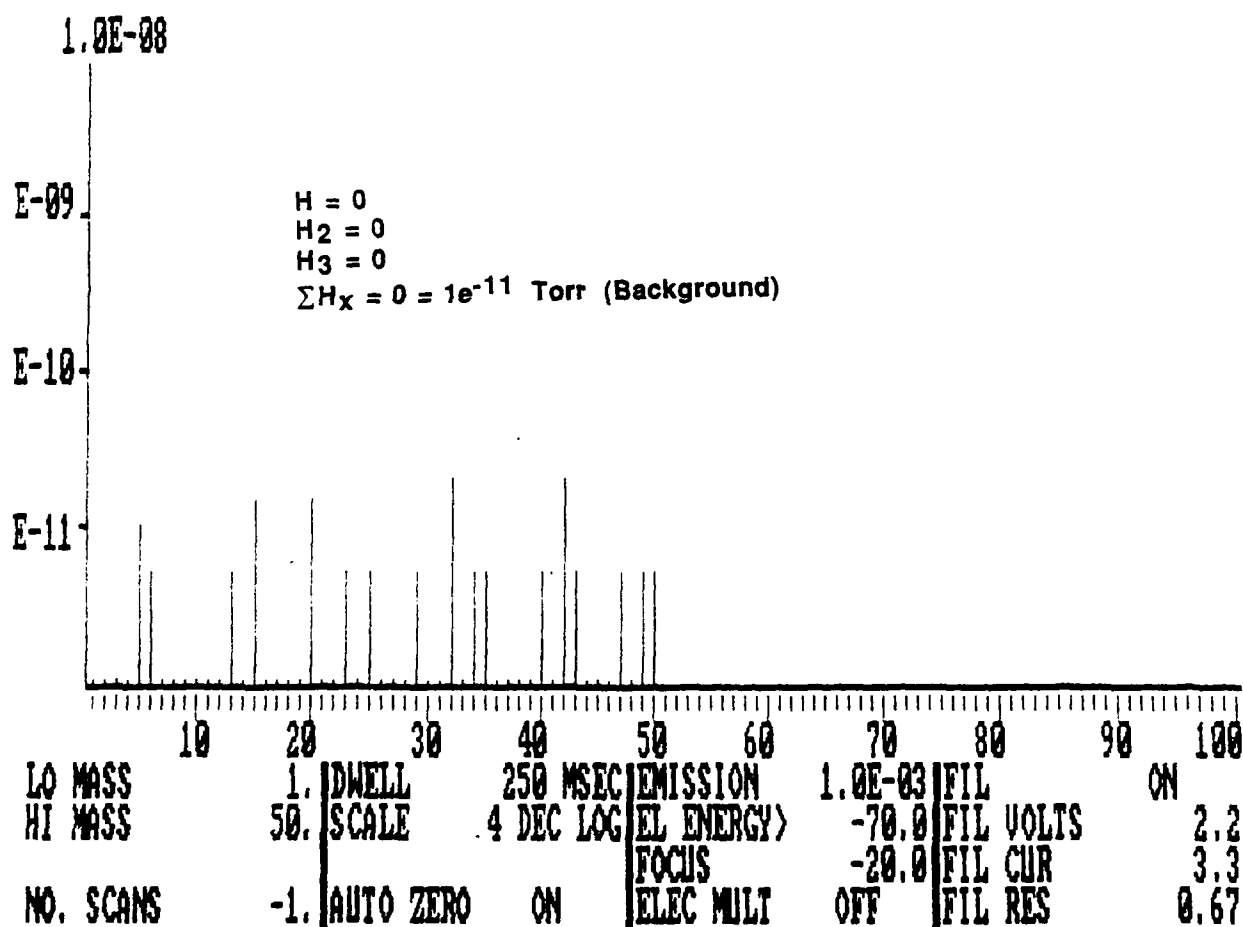


Figure D-6. Stability Test. T = +24 hr.

TOTAL PRS 7.5E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 9/89 8:17

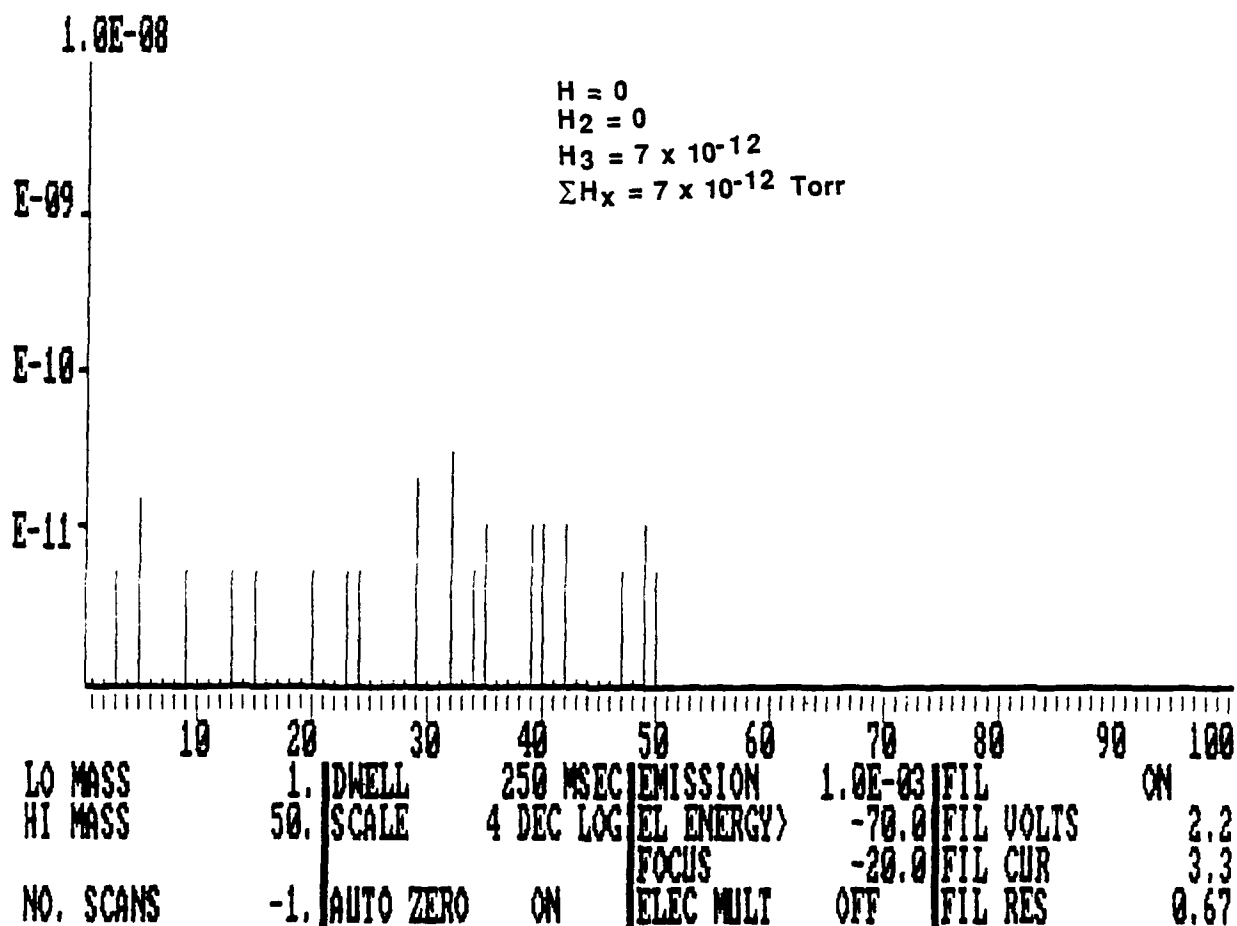


Figure D-7. Stability Test. T = 0 hr.

TOTAL PRS 7.5E-09 DISP SPEC A-B SCAN SPEC A 2/ 9/89 9:17

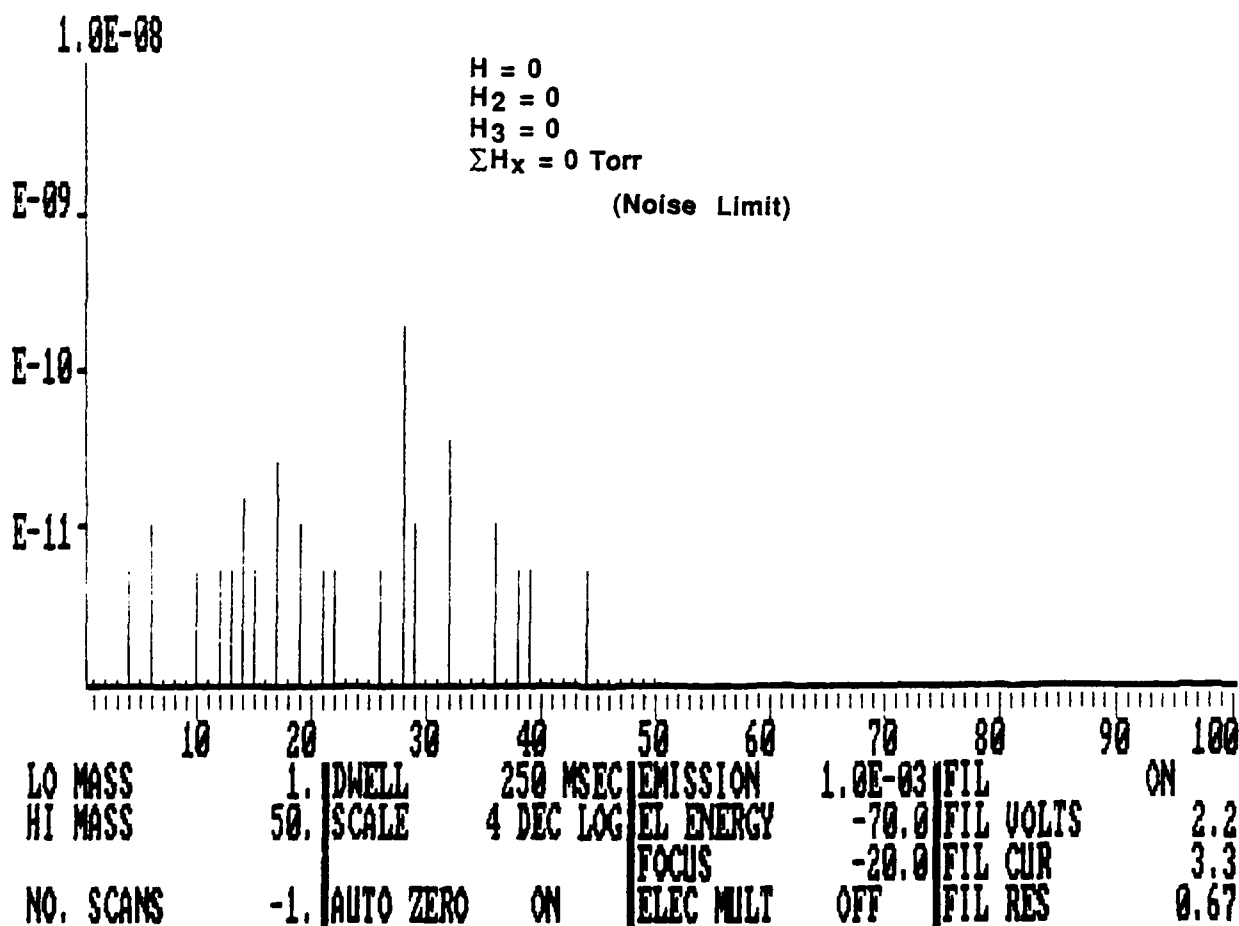


Figure D-8. Stability Test. T = +1 hr.

TOTAL PRS> 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/ 9/89 16:16

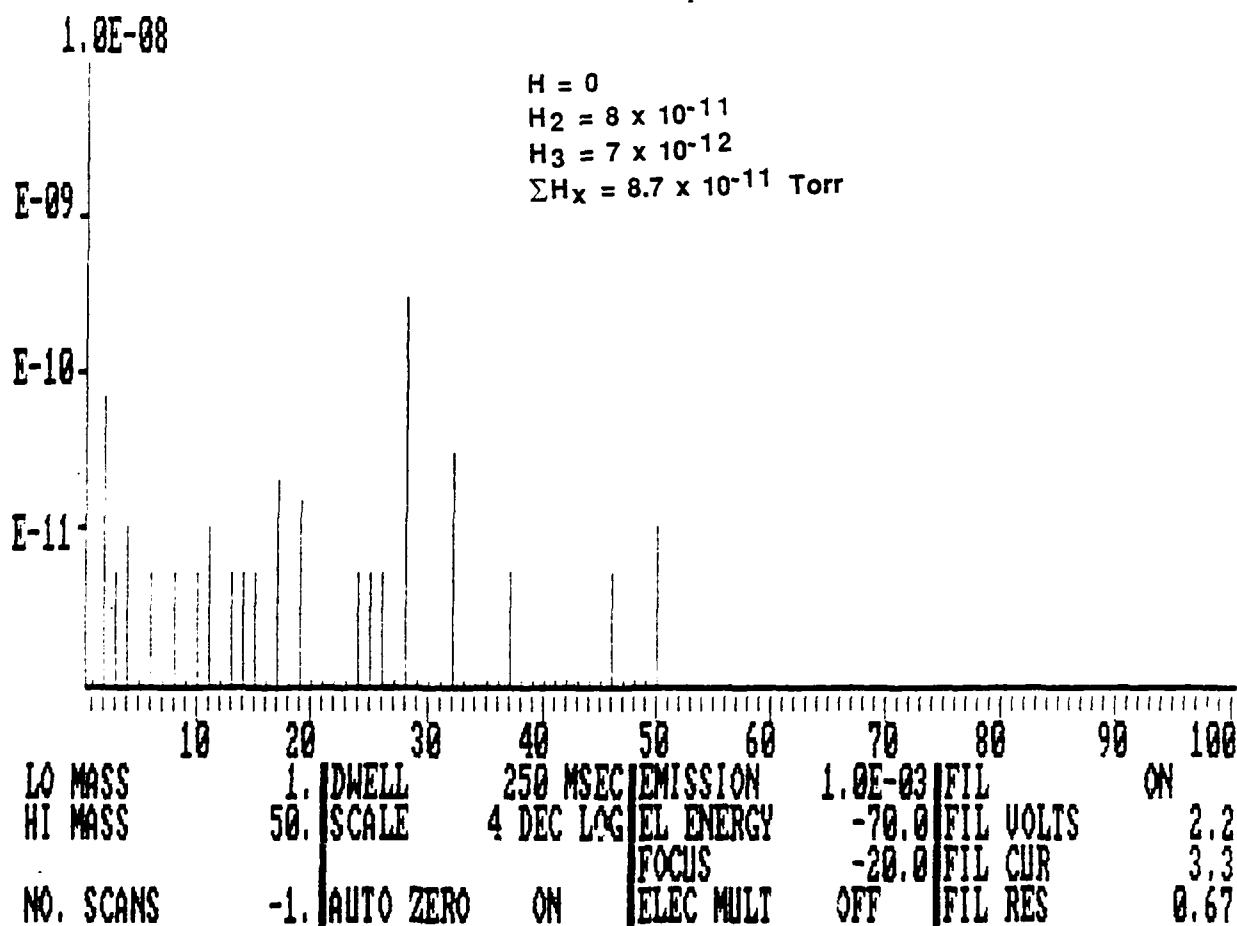


Figure D-9. Stability Test, T = +8 hr.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A 2/10/89 8:15

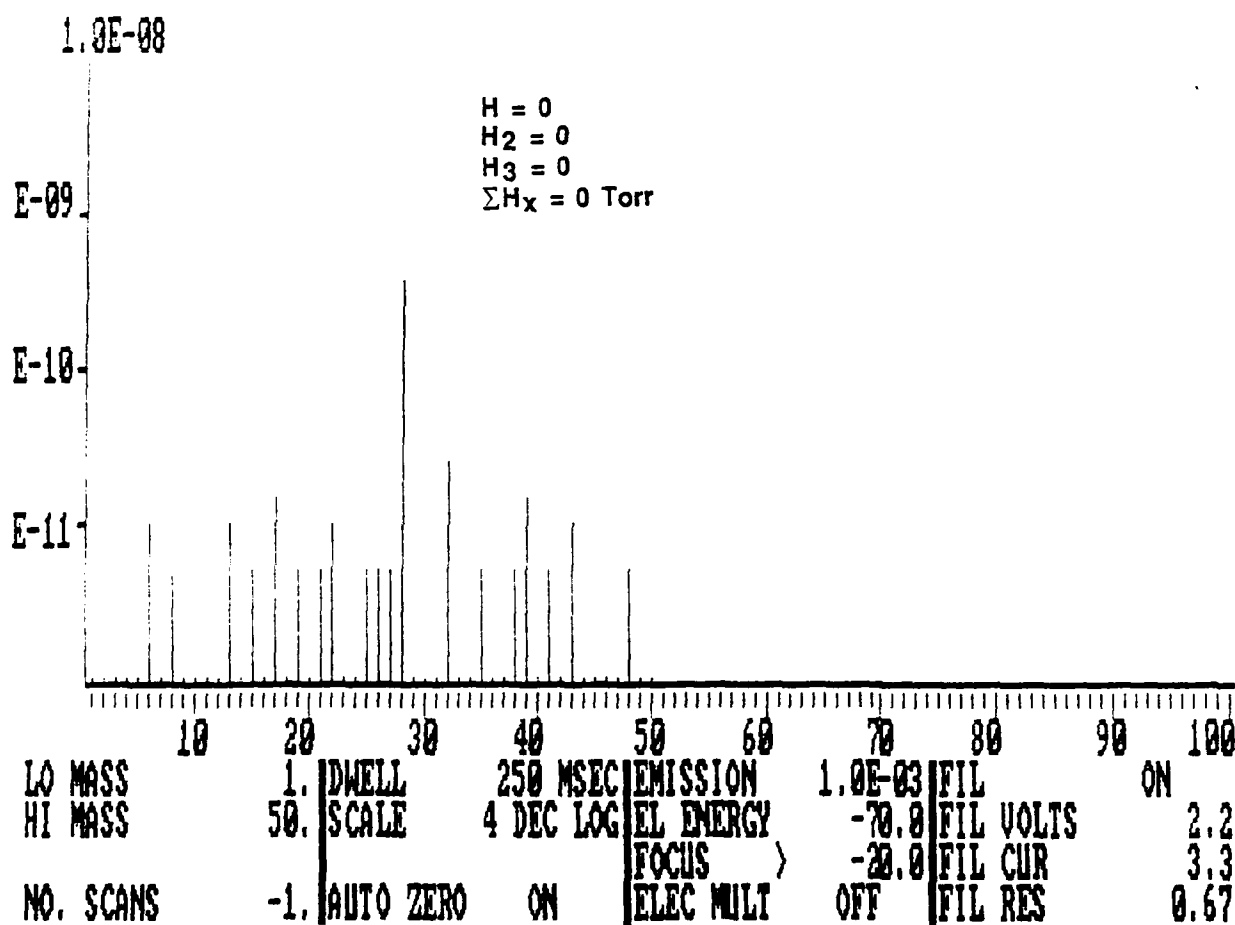


Figure D-10. Stability Test. T = +24 hr.

TOTAL PRS 7.4E-09 DISP SPEC A-B [SCAN SPEC] A | 2/11/89 10:47

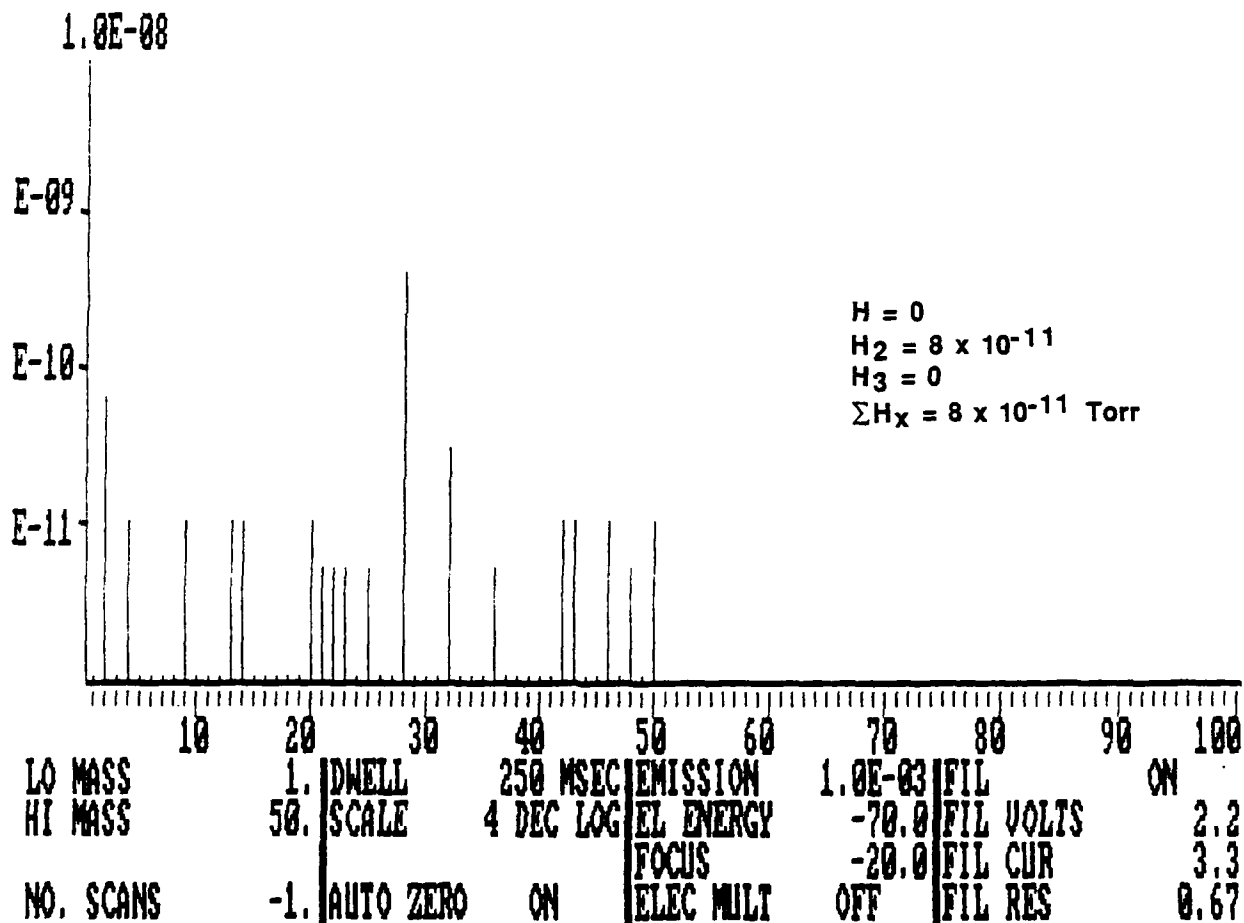


Figure D-11. Stability Test. T = 0 hr.

TOTAL PRS 7.5E-09 | DISP SPEC A-B | SCAN SPEC A | 2/11/89 11:45

> 1.0E-08

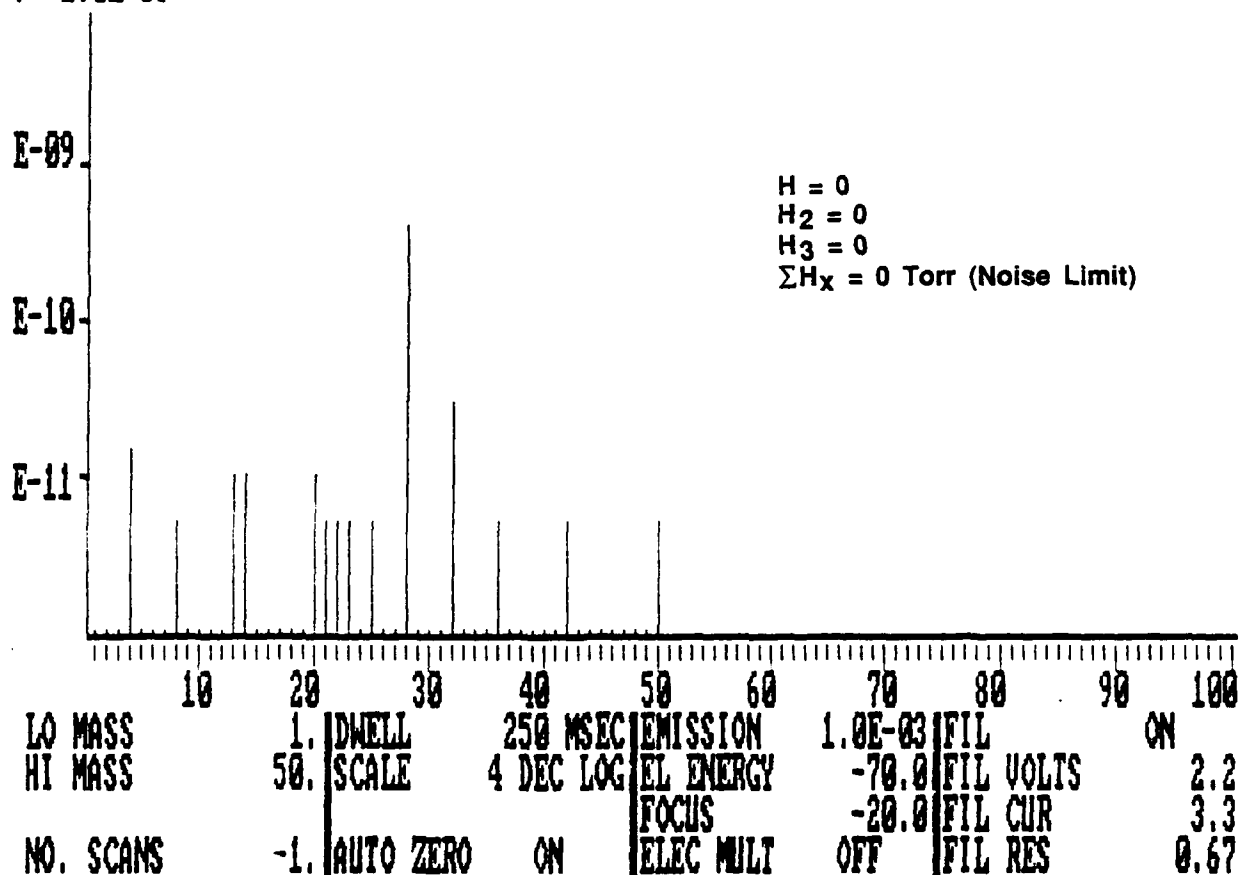


Figure D-12. Stability Test. T = +1 hr.

TOTAL PRS 7.3E-09 DISP SPEC A-B SCAN SPEC A | 2/11/89 18:44

> 1.0E-08

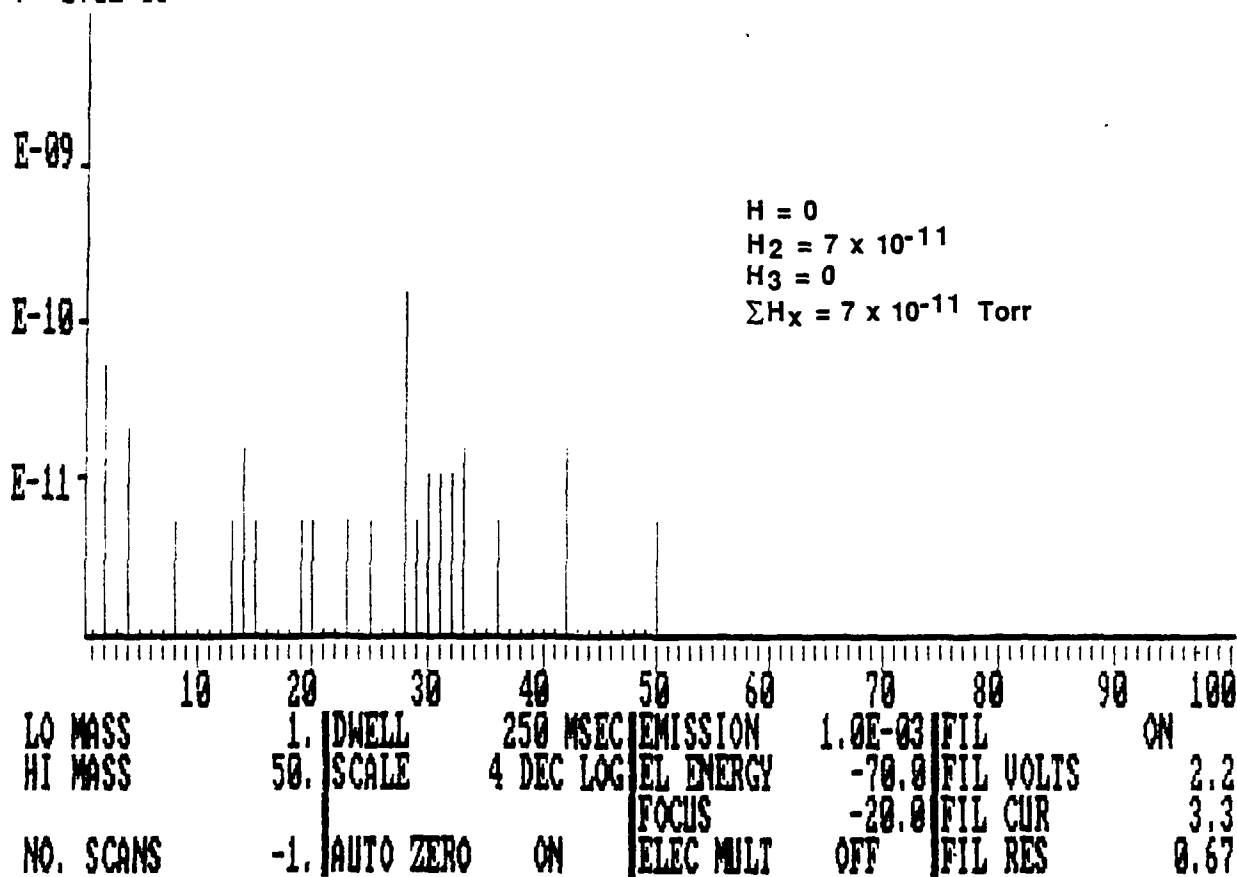


Figure D-13. Stability Test. T = +8 hr.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/12/89 10:46

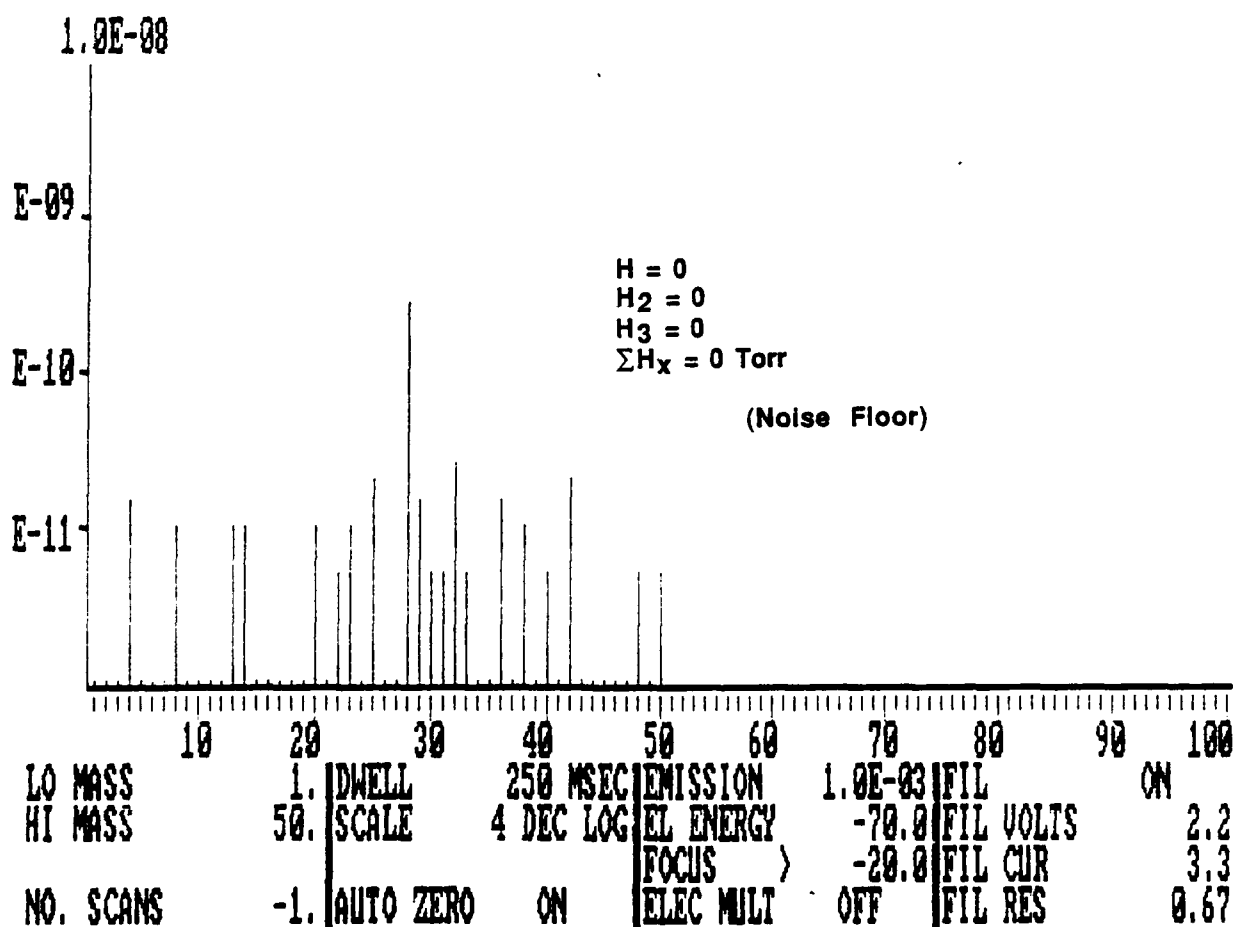


Figure D-14. Stability Test. T = +24 hr.

TOTAL PRS 7.3E-09 | DISP SPEC A-B | SCAN SPEC A | 2/15/89 8:15

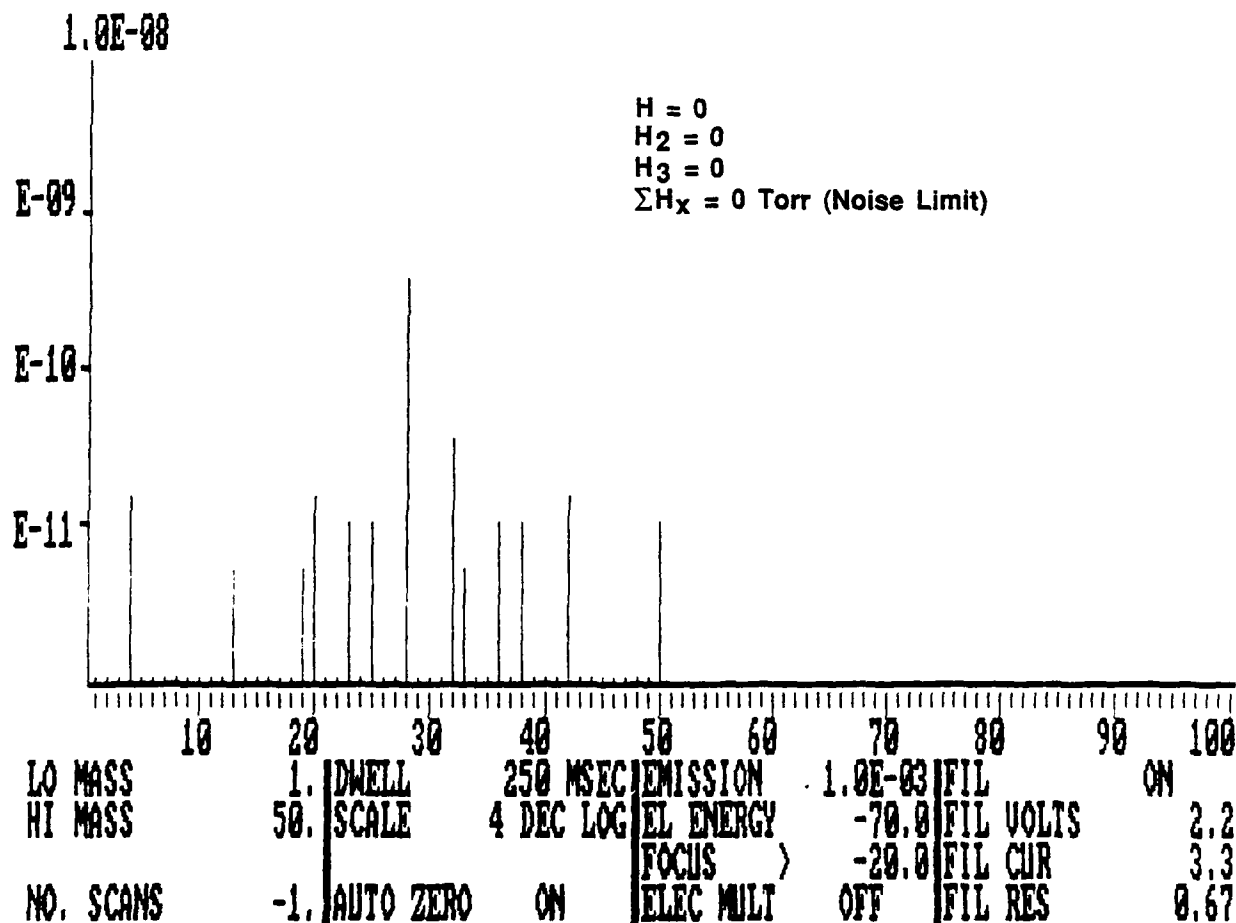


Figure D-15. Stability Test. T = 0 hr.

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/15/89 9:14

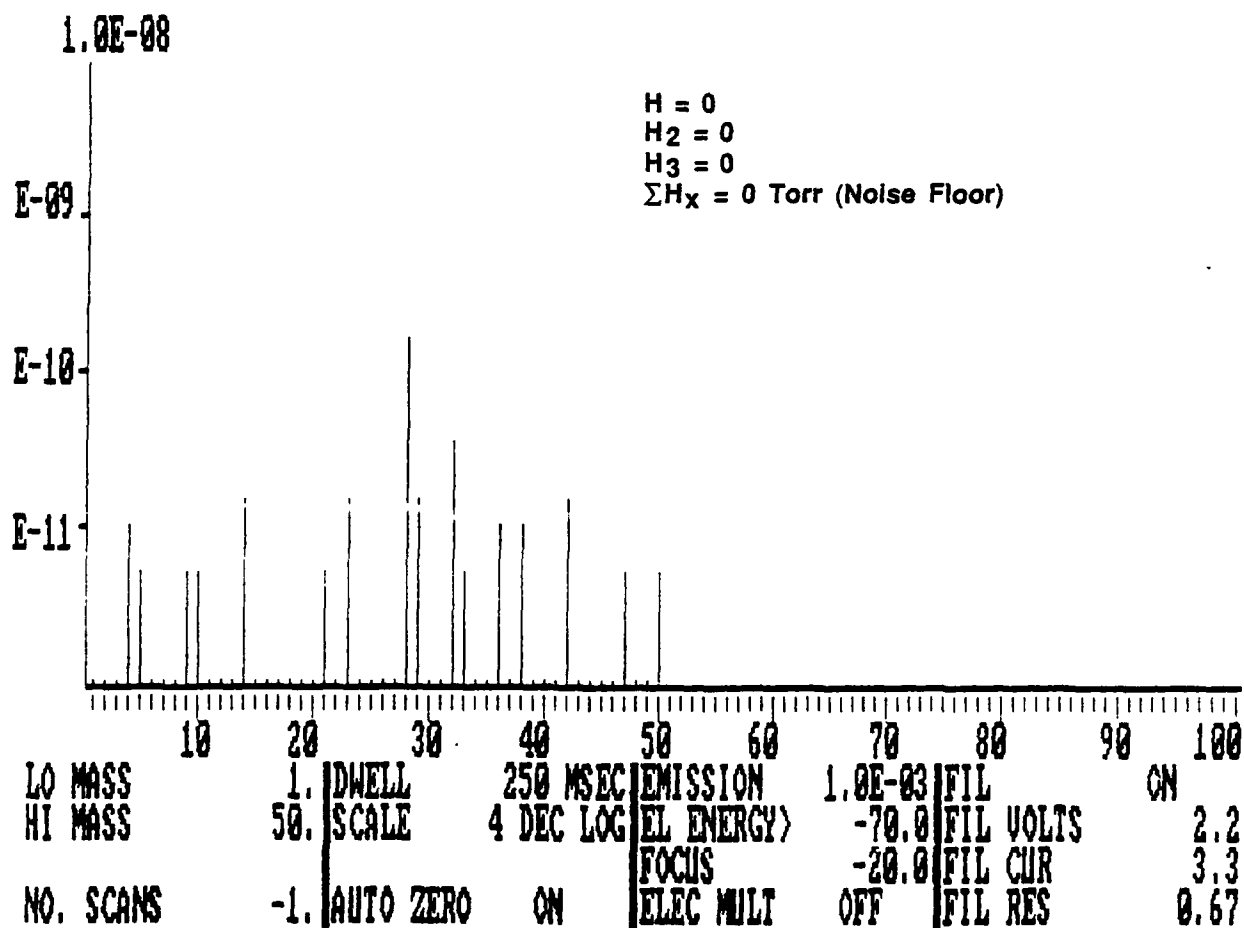


Figure D-16. Stability Test. T = +1 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/15/89 16:19

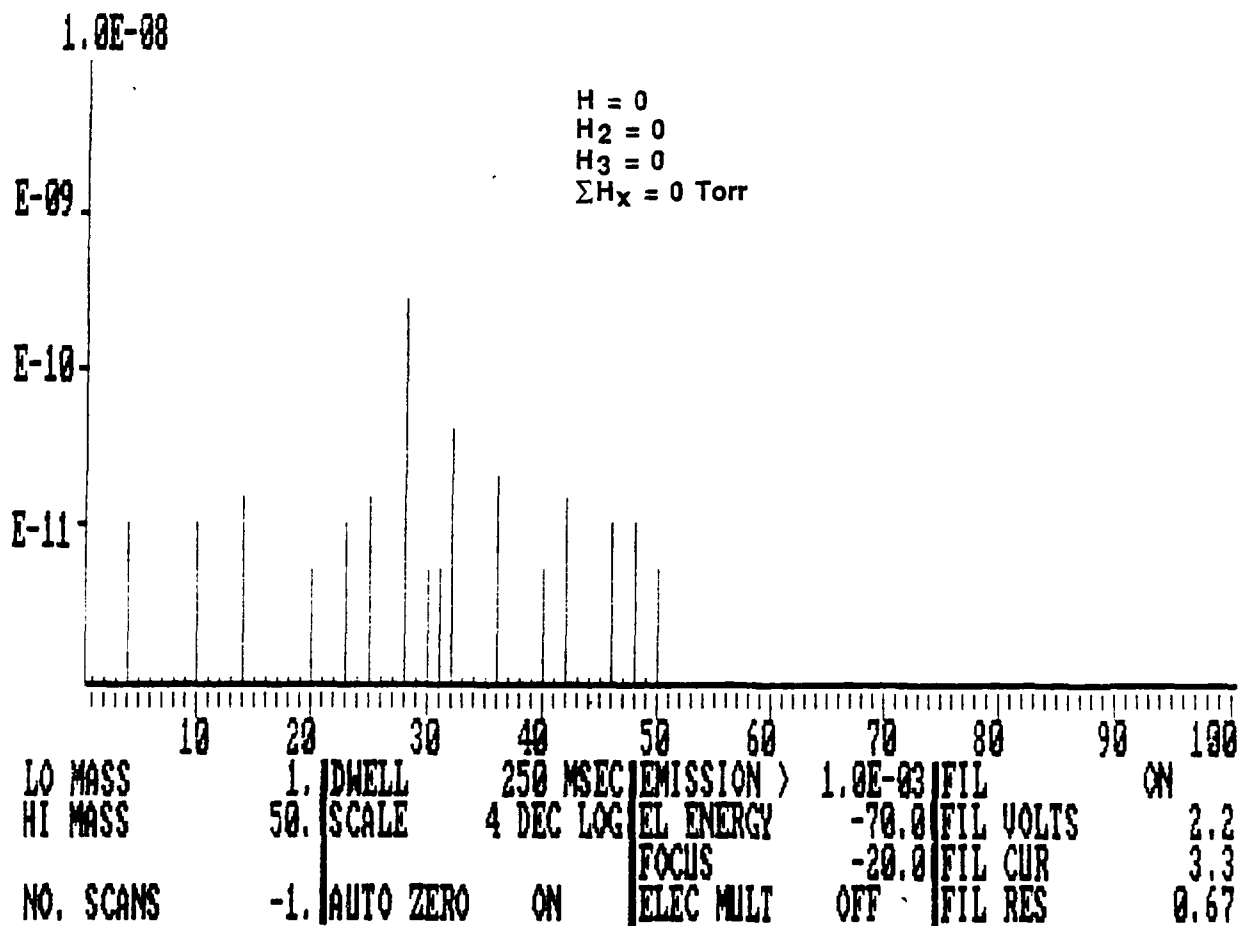


Figure D-17. Stability Test, T = +8 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/16/89 8:15

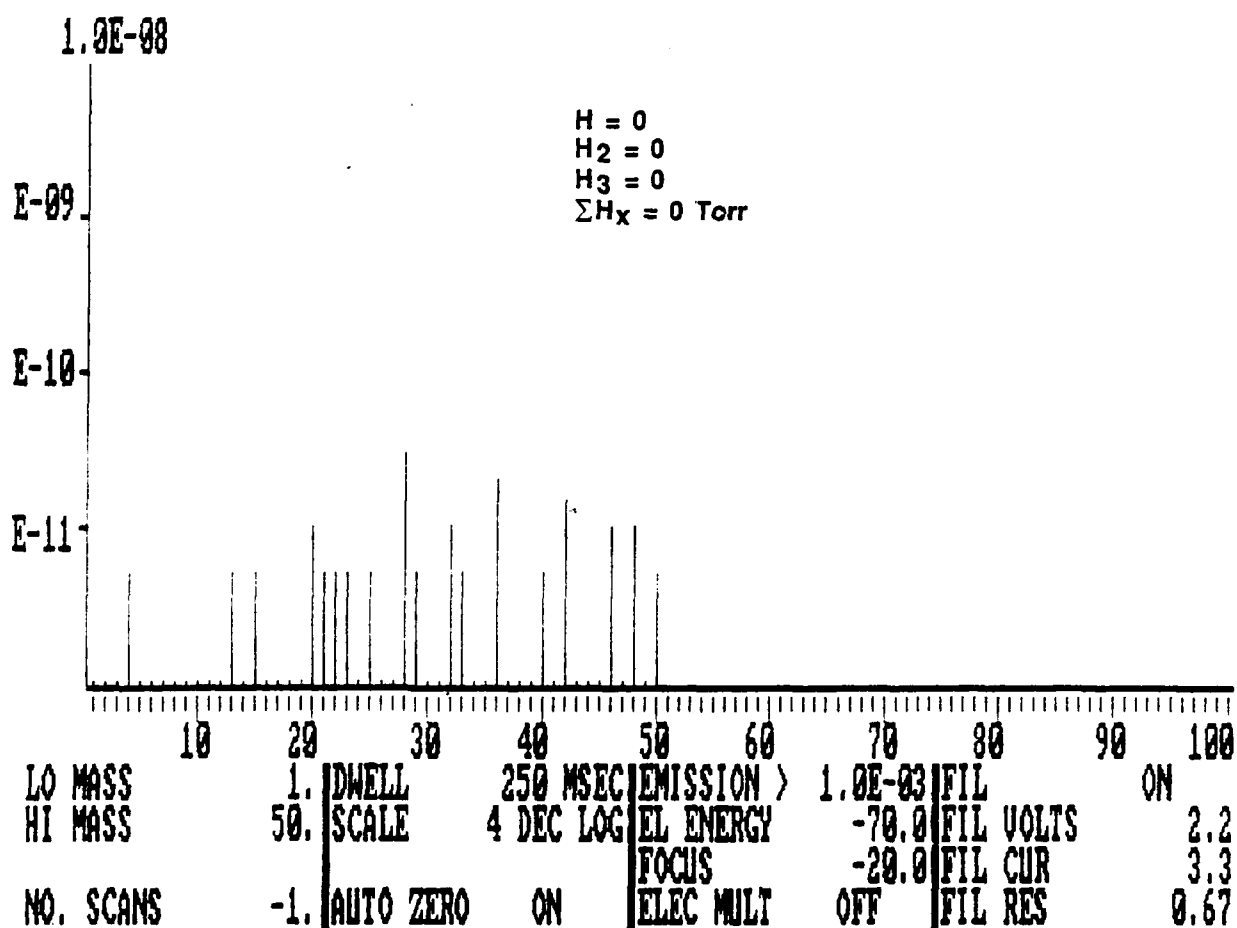


Figure D-18. Stability Test. T = +24 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/17/89 8:25

> 1.0E-08

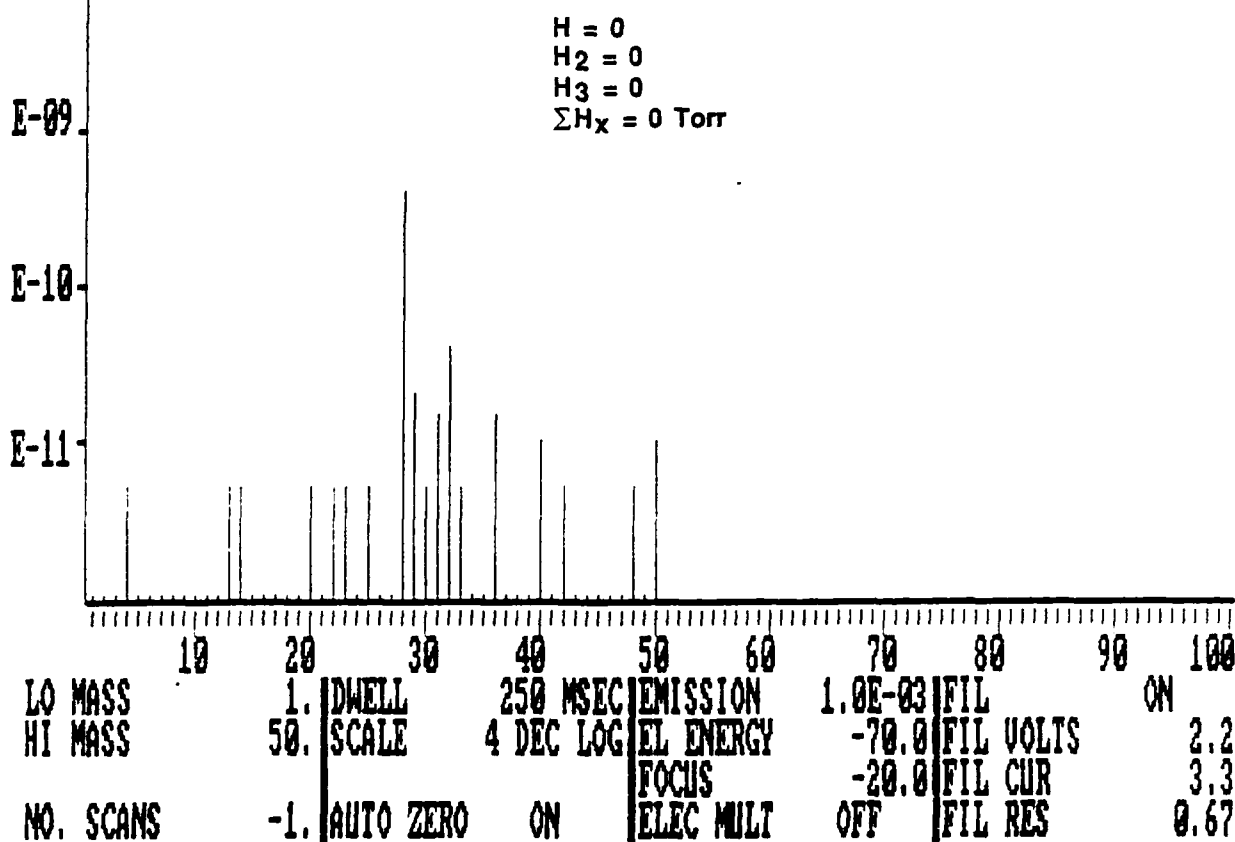


Figure D-19. Stability Test. T = 0 hr.

TOTAL PRS 7.4E-09 [DISP SPEC] A-B [SCAN SPEC A | 2/17/89 9:18

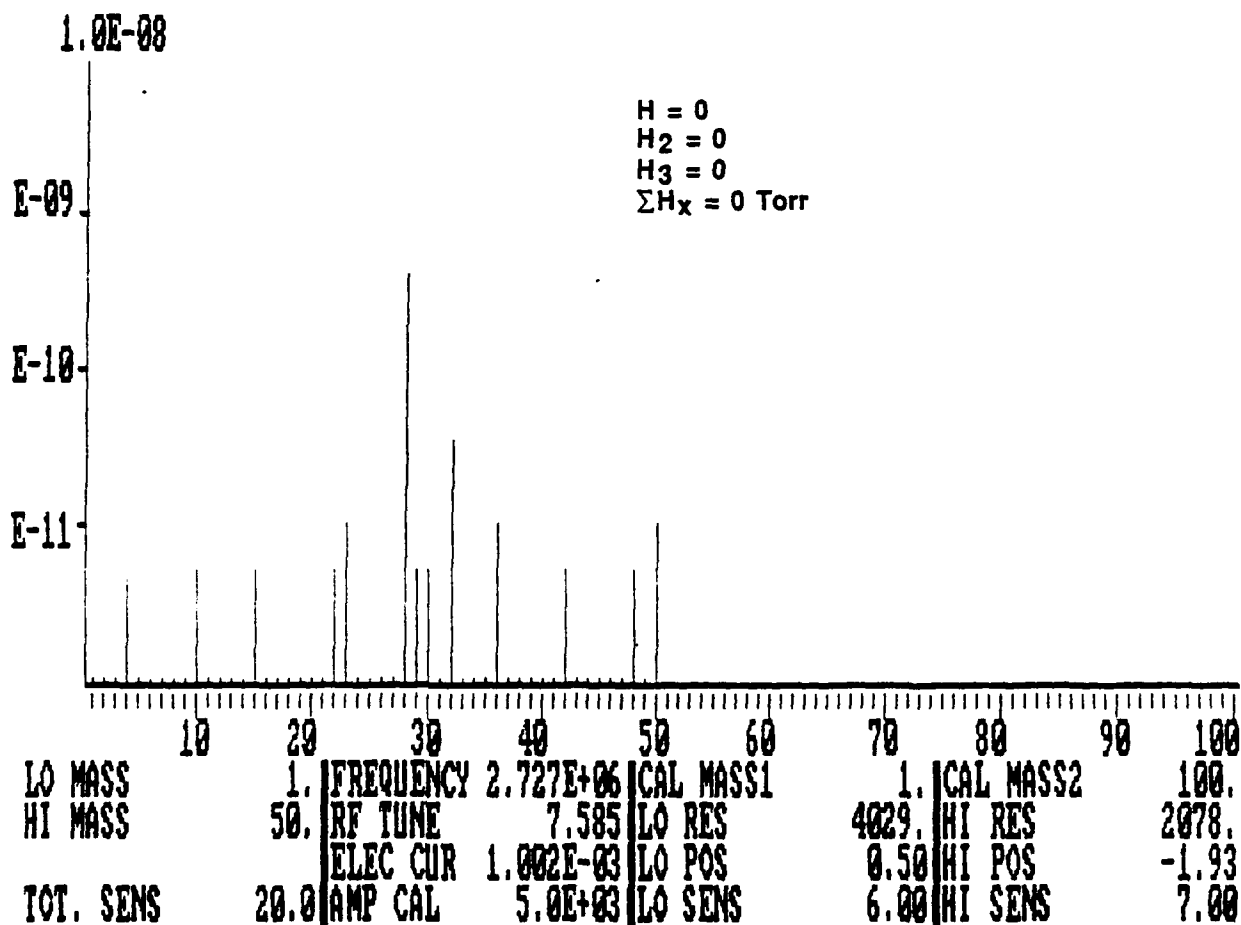


Figure D-20. Stability Test. $T = +1 \text{ hr.}$

TOTAL PRS 7.4E-09 DISP SPEC A-B SCAN SPEC A | 2/17/89 16:15

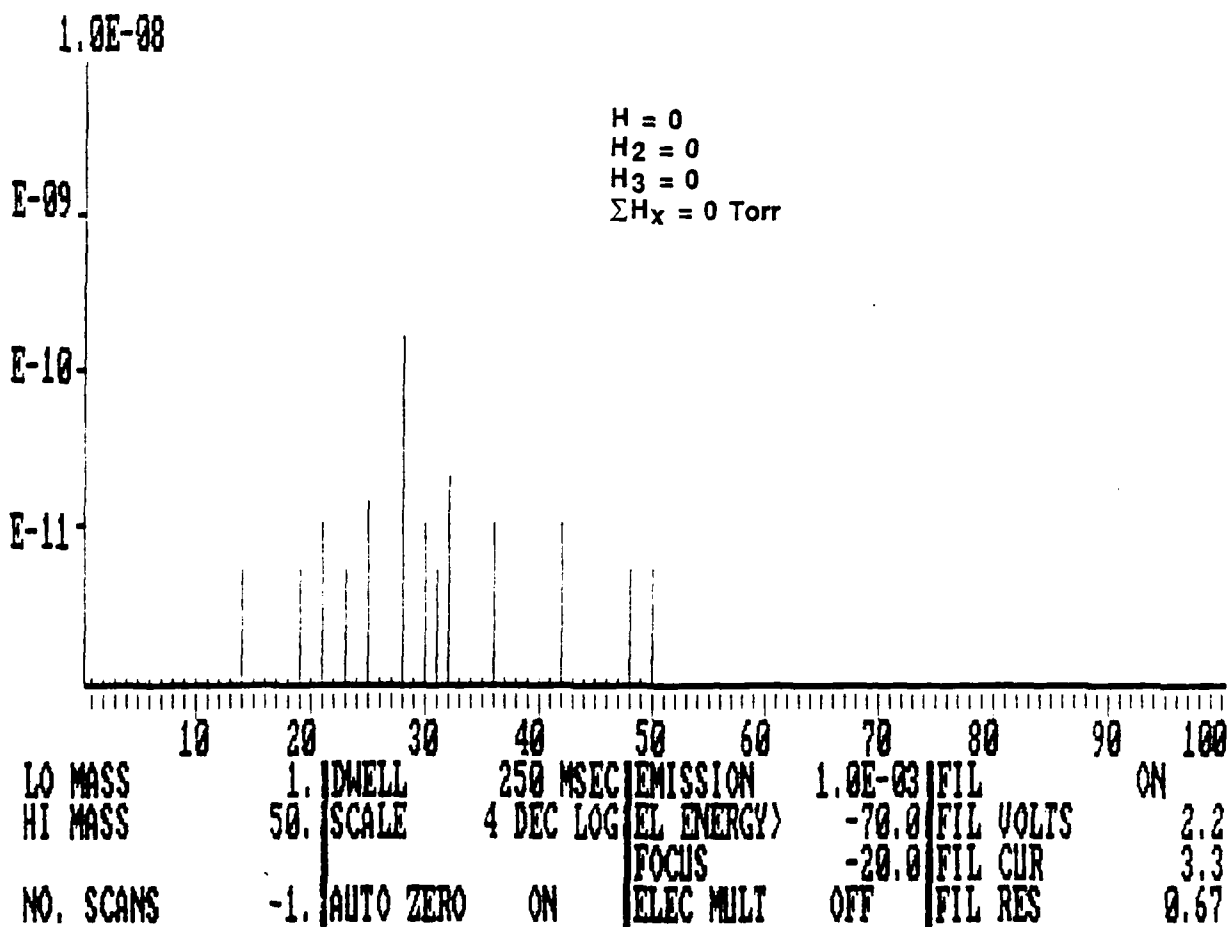


Figure D-21. Stability Test. T = +8 hr.

TOTAL PRS 7.4E-09 | DISP SPEC A-B | SCAN SPEC A | 2/18/89 8:16

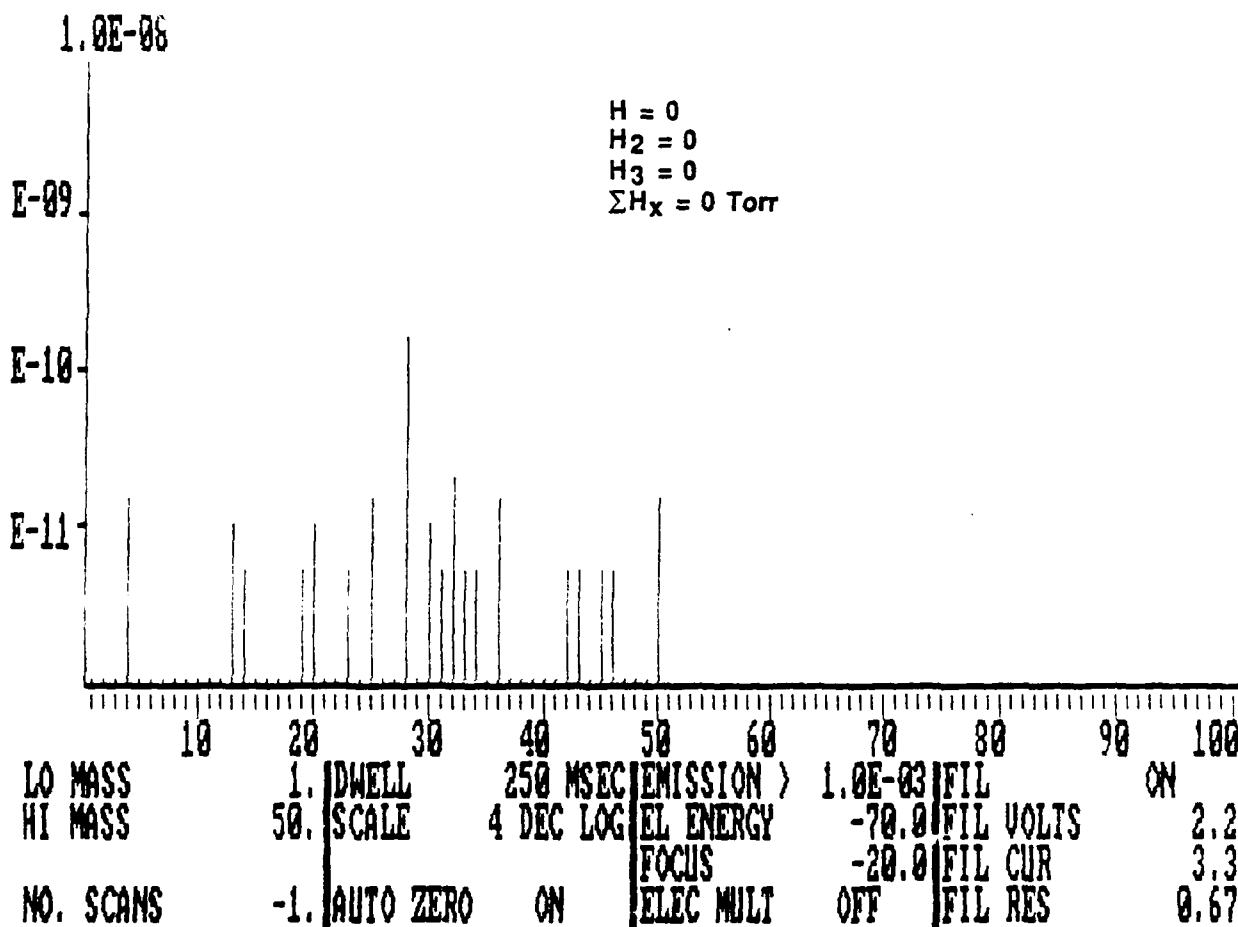


Figure D-22. Stability Test. T = +24 hr.

APPENDIX E

PROPELLANT CORROSION RESISTANCE STUDY (AL)

Astronautics Laboratory (AFSC)
LSSP
Edwards AFB, CA 93523-5000

Physical Science Research Section Report

Report No. 105-89 Date Mailed: 15 AUG -89
Suffix: 2V Requester: CURT SELPH/5168 Address: RKLC

Sample Description:
DIAMOND FILM

Analysis Requested:
COMPATABILITY WITH N₂O₄/CLF₃/N₂H₄

Analyst: T. W. OWENS Manhours: 20

Analyst: L. A. DEE Manhours: 2

Approved: Roy Wurzbach
Roy Wurzbach, Chief
Physical Science Research Section
(805) 275-5410
A/V 525-5410

The apparatus used for exposing the diamond film samples to ClF₃ and N₂O₄ vapor was made from aluminum tubing, fittings, and a clear sapphire tubing test section. The sapphire test section was where the sample was located so that it could be observed and video taped during the test. The entire apparatus was wrapped with thermostatically controlled heating tape. Samples were pre-heated to 170° F. under helium prior to being exposed to the gaseous oxidizers. Vapor exposure durations at 170° F. to both ClF₃ and to N₂O₄ were 20 minutes. Exposure duration to liquid N₂O₄ at 65° F. was for 30 minutes in a Pyrex vessel. Exposure duration to liquid N₂H₄ at 65° F. was for 24 hours in a Pyrex vessel.

Results:

Photo graphic evidence as well as "pre" and "post" sample weight data (± 0.000001 gram) showed that none of the diamond film samples that were tested for compatability with the subject propellants had undergone any observable change due to exposure to these fluids.

Conclusions:

The above compatability tests do not represent the final word on diamond film compatability with these propellants. These test conditions were not intended to duplicate the conditions of use for diamond films in propulsion systems. These tests were only intended to provide sufficient data to assess the value of conducting additional, more extensive tests at actual system operating conditions which are beyond the capabilities of this organization. Our tentative compatability data indicates that further tests are warranted.