DIAMOND AS A MICROELECTRONICS MATERIAL WITH POTENTIAL FOR SPACE APPLICATIONS

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Nearly ten years ago the National Security Agency's Laboratory for Physical Sciences (LPS) in College Park, Maryland, began investigating the use of industrial diamond for thermal management of electronic assemblies. To achieve ultra-high computing speeds through the reduction of signal path lengths, they would have had to condense a 20 kW computer into a 15 cm/side cube, creating a 6 W/cm^3 thermal density. The excellent electrical, mechanical, and thermal properties of diamond made it an obvious choice for conducting the large amount of heat out of this cube, so the LPS incubated the growth of the chemical vapor deposited (CVD) diamond industry in this country. The LPS subsequently published several papers on the performance of CVD diamond as a component of electronic packaging. What they have not studied is the use of CVD diamond in space applications, where charged particles are in abundance. This report is intended to provide insight into the electrical, mechanical, and thermal properties of CVD diamond which make it so attractive for use in electronic packaging and into the questions which remain about its suitability for space flight applications.

Diamond is mechanically one of the strongest materials known and has very high dielectric strength. Its coefficient of thermal expansion (CTE) is on the order of silicon's, and its thermal conductivity is unmatched. These properties are all related to the strength of the carbon bonds in the crystal and its structure. For illustrative purposes, Table 1 shows room temperature values for the properties of materials often used in electronic packaging

Table 1. Properties of Electronic Device & Packaging Materials*

Material	Young's Modulus (10^{12}dynes/cm^2)	Electrical Resistivity (Ω-cm)	CTE (10^{-6}/°C)	Thermal Conductivity (W/cm-°C)
Single Crystal Diamond	10.5	10^{16}	1.2	22
CVD Diamond	8.40	10^{14}	2.0	21
Beryllium Oxide	1.01	10^{14}	7.4	2.4
Aluminum Nitride	1.81	10^{14}	3.2	2.2
Silicon	1.13	10^{3}	3.0	1.5
Copper	1.10	1.7×10^{-6}	16.8	3.8
Gold	0.79	2.4×10^{-6}	14.3	3.1
Kovar	1.33	3.6×10^{-6}	5.3	0.39

*These values have a strong dependence on temperature and where those dependencies affect CVD diamond's performance in electronic packaging applications, it is noted in this paper. The reader should refer to the published literature on materials and diamond (natural and CVD) for more in-depth discussions on material properties and techniques for measuring them.

Twenty years ago, industrial diamond was manufactured using high pressure, high temperature methods which were expensive and produced only a few individual grains of diamond. A low-pressure method that allowed the fabrication of diamond films and wafers through chemical vapor deposition was developed in the early 1980's. This new method reduced the cost dramatically by significantly increasing the growth rate. The cost is still falling.

CVD diamond can be processed using several methods (see Table 2). A substrate such as silicon or ceramic is exposed to a plasma of hydrogen (or oxygen) and a carbon-containing reagent such as methane (CH_4). The ionized hydrogen first attaches to the substrate then combines with CH_4 radicals leaving diamond, diamond-like-carbon (DLC), and graphite crystals behind[**].

Table 2. Established Methods for Producing CVD Diamond Films[**]

Method	Gas Pressure	Substrate Temperature (°C)	Filament Temperature (°C)	Power	Deposition Rate (μm/h)
Hot Filament	10 - 100 torr	700 - 1000	2000 - 2400	-	0.3 - 40
Plasma Assisted: Microwave	10 - 100 torr	800 - 1100	-	600 - 1500 W	0.1 - 30
Plasma Assisted: DC Plasma Jet	60 - 760 torr	800 - 1100	-	1 - 50 kW	10 - 930
Flame	~ 1 atm	800 - 1100	-	-	30 - 200

** See Diamond Chemical Vapor Deposition Nucleation and Early Growth Stages, by H. Liu and D.S. Dandy [3] for a good explanation of processes that are used to manufacture CVD diamond films.

Depending on the temperature and pressure used in the CVD process, either a highly ordered or a columnar structure can occur. The columnar structure is easier to manufacture, but it allows more sites for non-diamond carbon and non-carbon defects to occur. The elements in the gasses used to create the diamond, and in the materials that make up the chamber assembly, also affect the way the crystal grows and the type and the amount of defect sites that are present in the resulting material. The reduction in electrical, mechanical, and thermal performance of CVD diamond films is directly related to the number and types of defect sites contained in the material.

When the epitaxial growth is columnar, the electrical, mechanical, and thermal properties will differ between those in the direction of growth versus those in the direction across the plane of deposition. The thermal conductivity in the plane of the substrate can be 50% to 11% of its value perpendicular to the growth plane [4,5]. At 50%, thermal conductivity is still several times larger than that of competing substrate materials (see Table 1). In addition, the morphology at the substrate/diamond boundary where growth begins (the nucleation surface) will cause some differences in properties there versus those on the growth surface.

Crystal growth at the nucleation surface occurs first by accumulation of DLC crystals, then by diamond growth in the planar direction, and finally by epitaxial growth of diamond normal to the substrate plane. This results in much smaller grain sizes and smaller spaces between the grains on the nucleation side of the diamond film and larger grains and fewer, yet larger, spaces between the crystals on the growth side. Figures 1 and 2 illustrate the film growth pattern and the columnar morphology.
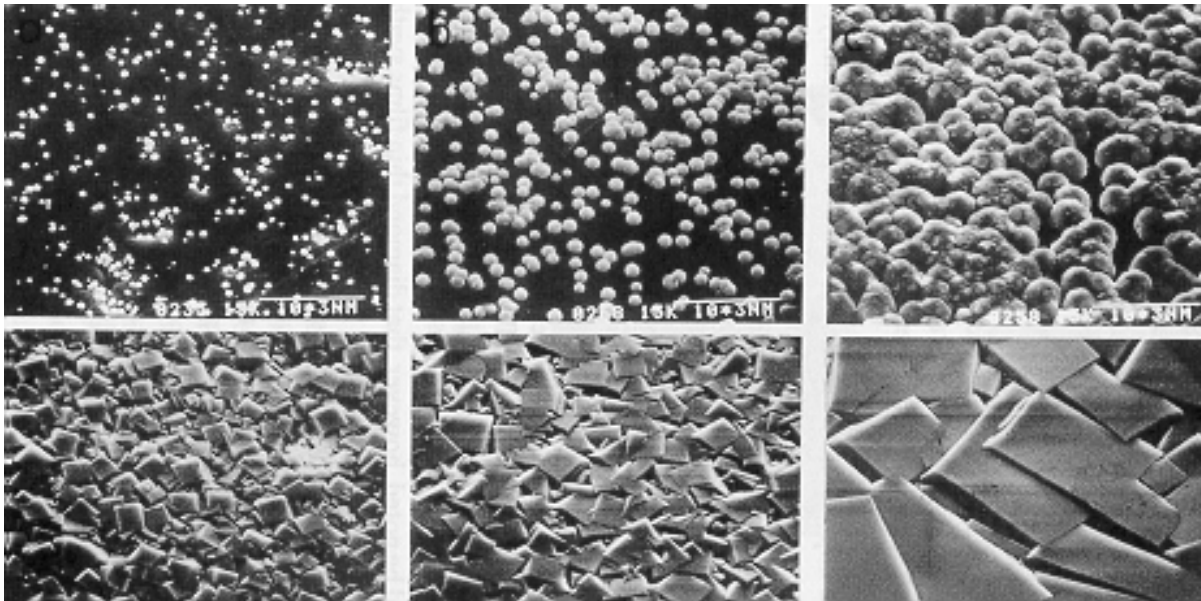

Figure 1. Growth of diamond film: from crystallites on the nucleation surface

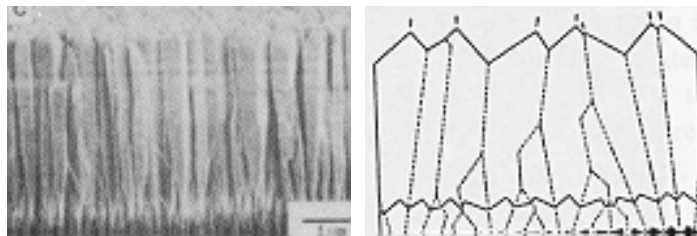*to the beginning of the growth of the ordered structure [3].*

Figure 2. Photograph and drawing of the columnar structure [3].

Yield losses are dominated by cracking in the diamond film due to several design and process factors such as the choice of substrate material, the diameter to thickness aspect ratio, and thermal gradients between the front and back faces of the substrate and across the surface of the substrate. Although a substrate/CVD diamond wafer can exhibit a high degree of flatness, that flatness can be lost when the substrate is removed (by grinding or etching). Grinding or polishing the diamond can be used to restore the flatness. Table 3 shows specifications for commercially available (from Diamonex) substrates.

Table 3. CVD Diamond Substrate Specifications

Diameter	0.5 mm-15 cm
Thickness	1-1000 μm (300 μm typical)
Tolerance	±0.001 cm
Surface Flatness	<5 μm/cm

The extraordinary properties of this material have driven industry to improve the CVD process. Ten-inch diameter wafers are now grown in days, with yields greater than 95%, and at a very affordable price. 12" and 15" wafers will soon be available.

Diamond is a crystalline material with no dangling bonds within the bulk material. There are, however, dangling bonds when the crystal pattern is terminated at a surface. These bonds cause the surface to rapidly accrete non-diamond substances (primarily hydrogen) from the environment. The bonds are covalent; therefore, large energies are required to break them, making adhesion of circuit traces and element problematical.

The first attempts made to metallize diamond films used traditional thin and thick film processes. The lack of dangling bonds on the diamond surface caused the metal to peel off. A process was developed by the LPS which, by high temperature baking, provides a surface on the diamond which is able to both chemically and mechanically bond to both metal and dielectric films.
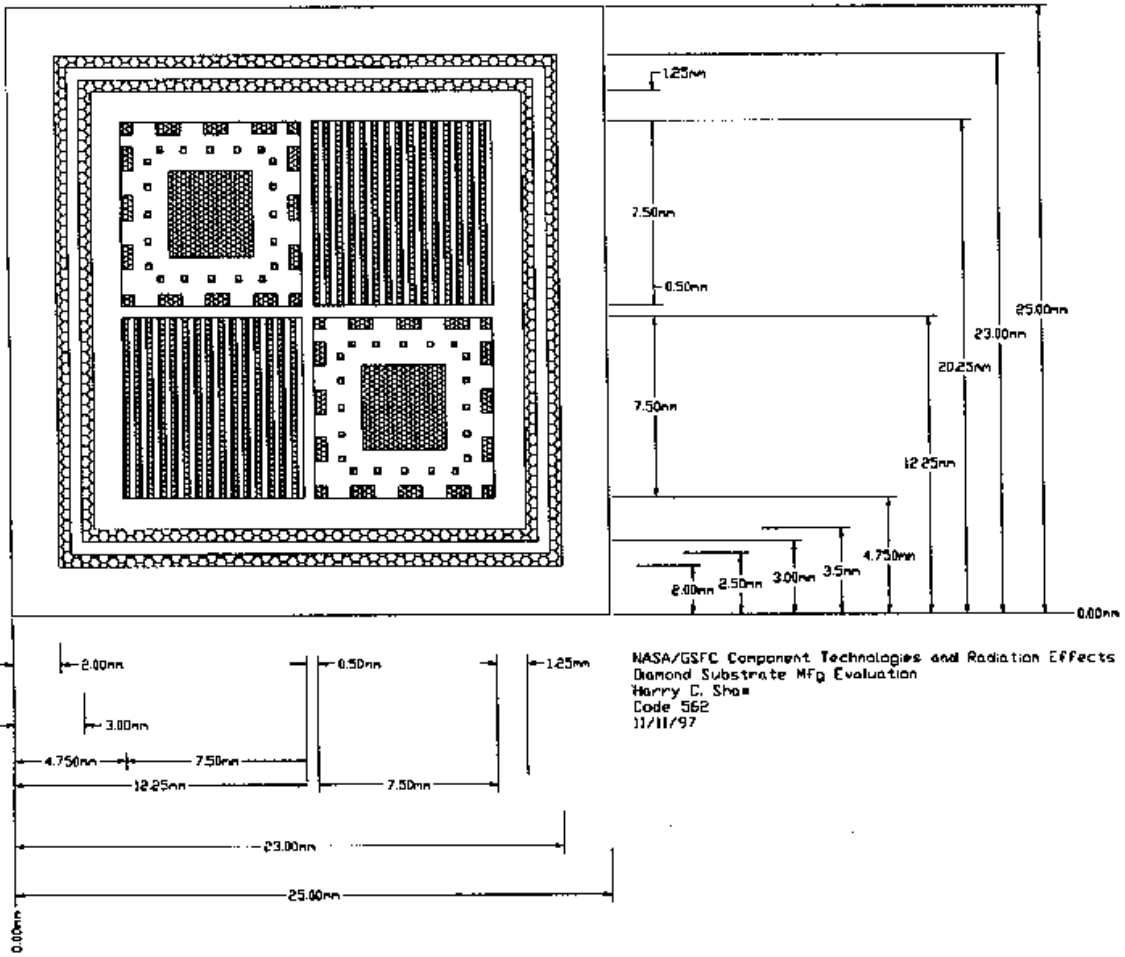
The reliability of the metal attachment to the diamond film is higher for the growth side of the diamond film, because the very small grains on the nucleation surface more easily brake away from the bulk material than the large grains on the growth surface [9]. The diamond surface suffers no damage from multiple exposures to etchants used to remove the gold and dielectric deposits, showing that diamond substrates can be reliably stripped and re-metallized.
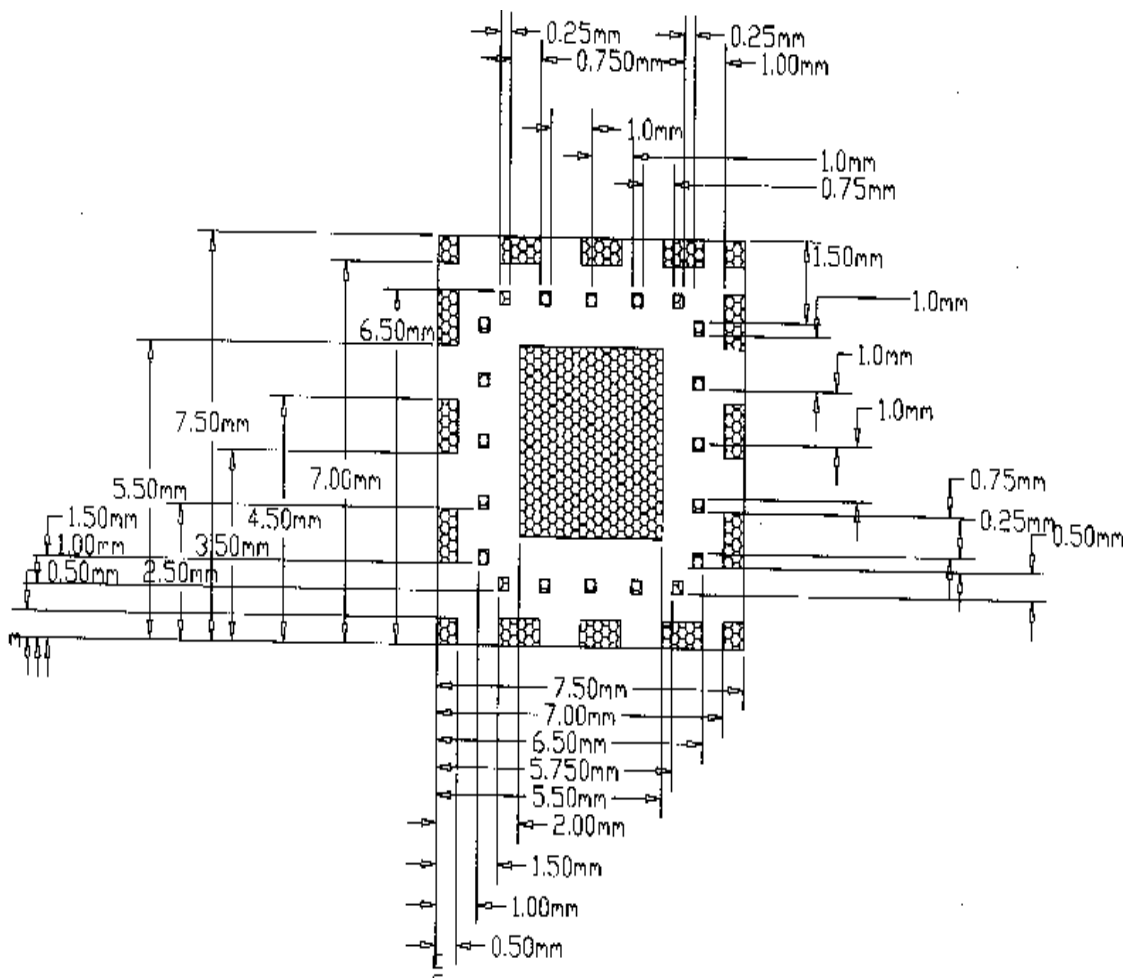
Although through-holes can be drilled in CVD diamond using a laser (see below), the industry has not yet been able to metallize them, nor have they been able to manufacture multilayered (diamond and metal) printed circuit structures. Micro-machined structures have been fabricated using diamond, but the process is not yet competitive with those used to make silicon MEMS devices [11].

Crystalline Materials Corporation, Norton, and Diamonex are now supplying metallized diamond substrates for electronic applications. Samples were purchased from Diamonex for evaluation by NASA's Advanced Interconnect Program. Table 4 shows the specifications used to purchase the substrates. Figure 3 shows the dimensions of the metallization on these samples. Figure 4 is a photograph of the resulting product. Testing is planned in fiscal year 1999 with the intention of determining the discriminators, both through process inspection and product screening, that can be used to identify reliable metallization on CVD diamond.

Table 4. Specifications Used to Purchase Thin Film Diamond Substrates

Edge Dimensions	25 mm x 25 mm x 300 μm (± 25 μm)
Surface Polish	< 0.03 μm on top (mirror) <0.10 μm on bottom (matte)
Metallization	Top with pattern, bottom fully covered with metallization.

NASA/GSFC Component Technologies and Radiation Effects
Diamond Substrate Mfg Evaluation
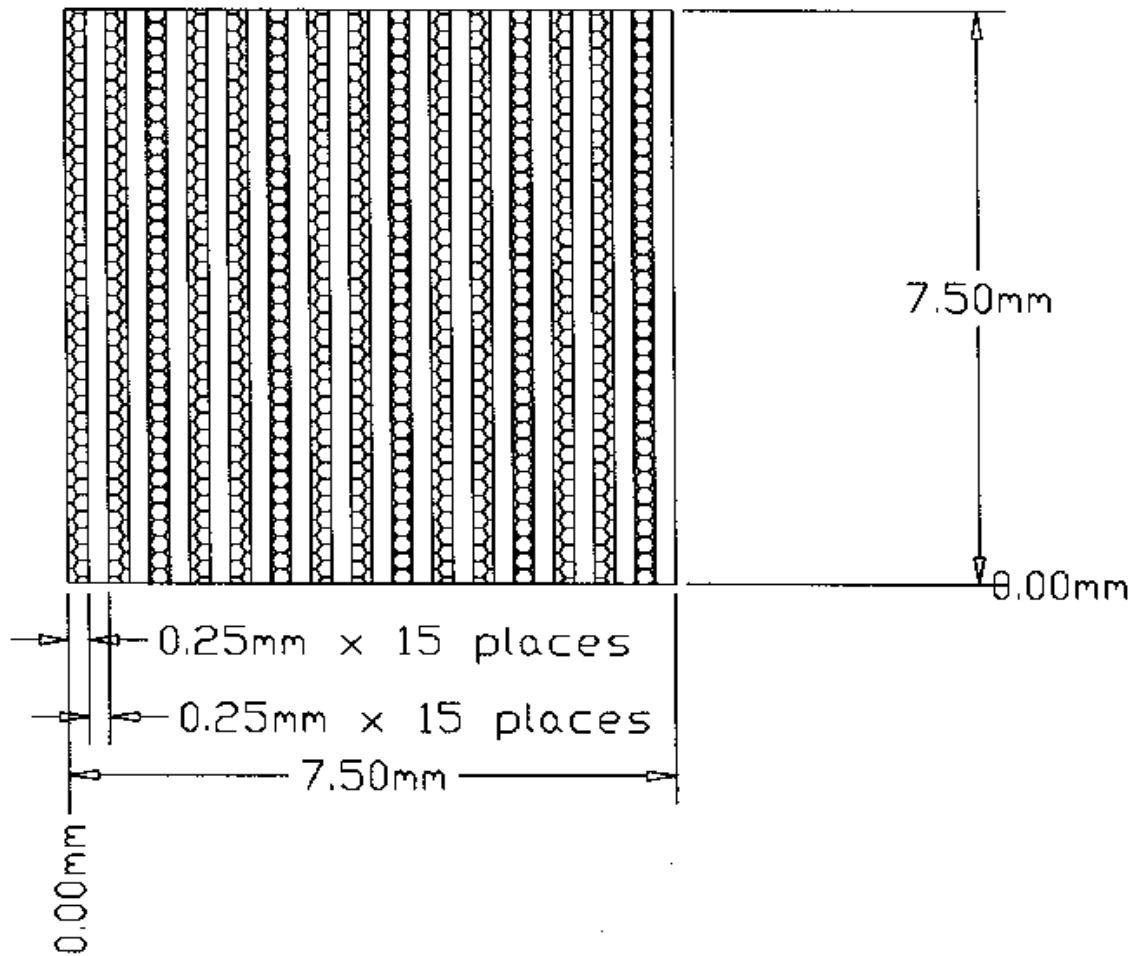Harry C. Shaw
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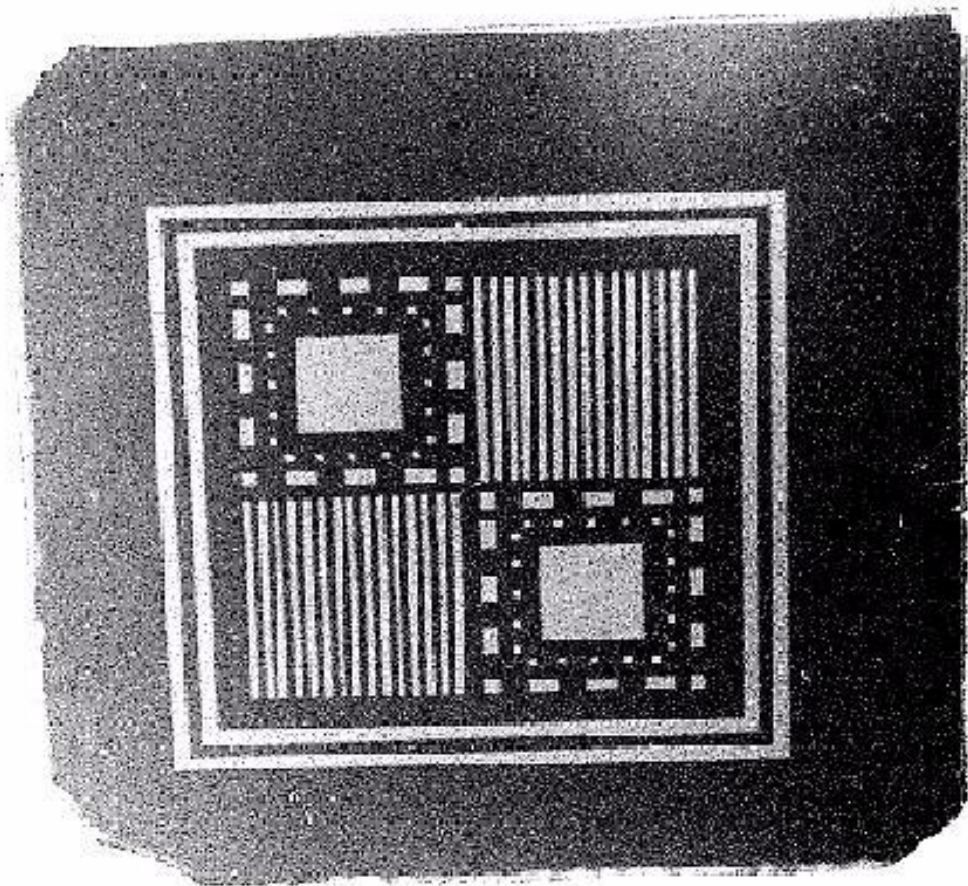*Figure 3. Dimensions of the Metallization on Diamond Samples*

Figure 4. Metallized Diamond Sample to be Evaluated

The LPS investigated laser drilling of holes in CVD diamond then measured the fracture strength of the drilled material. The results showed that, for films with a highly ordered crystal structure, holes drilled had the same diameter from start to finish, but, for films with a columnar morphology, the hole was larger on the nucleation side regardless of the drilling direction [10]. The nucleation side was found to be twice as strong as the growth side in point bending tests. The presence of drilled holes reduced that strength. The polishing or the beveling of edges had no effect on the strength. Columnar structures exhibited higher fracture strength than highly ordered structures. The LPS suggests that this may be evidence that the columnar material is experiencing plastic deformation before fracture [10].

The LPS discovered that resistive elements or paths can be "burned" into the diamond film. These paths behave as thermistors over a 0K to 450K temperature range [1,9]. At room temperature, the change of resistance with temperature was -15 mOhms/K, and the change in temperature with power was 1.1 K/W [9]. Experiments by the LPS showed that the highest quality graphite was that which was formed deepest in the film [9]. Table 5 shows the conditions required for laser cutting diamond films and for forming thermistors.

Table 5. Parameters for Laser Processing Diamond Film [9]

Parameter	For Cutting	For Making Thermistors

Laser Power (avg.)	1.6 W	1.0 W
Pulse Frequency	1 kHz	5 kHz
Feed Rate	0.2 mm/s	1 mm/sec

The LPS performed evaluations on flat-pack and pin grid array packages using CVD diamond as both a heat spreader within the package and a heat sink on the top of the package. In both cases, the thermal gradient between the device junction and ambient and between the substrate and ambient decreased by 50% [1]. This work supports the use of diamond inserts in traditional packaging configurations and for thermal management in vertically stacked assemblies.

Diamond is wide band gap material (see Table 6) [2]. Energies of 13 eV to 16 eV are required to create electron-hole pairs in it. The band-to-defect recombination mechanism dominates, and a carrier lifetime of a few hundred picoseconds makes the diffusion length less than a micron. Natural diamond and CVD diamond have been used in radiation detector applications. Their high carrier mobilities and carrier velocities provide quick response times, and, for a given radiation energy, the current resulting in diamond will be smaller than that resulting in a detector made with silicon or germanium allowing it to withstand higher energy radiation without permanent damage. Diamond's dielectric strength, depending on the quality of the material, is in the MV/cm range [11]. Table 6 compares the electronic properties of diamond and silicon.

Table 6. Electronic Properties of Silicon and Diamond at Room Temperature [11]

Property	Silicon	Diamond
Bandgap (eV)	1.12	5.47
Intrinsic Resistivity (Ω -cm)	10^5	$>10^{15}$
Breakdown Strength (V/cm)	3×10^5	$1 - 20 \times 10^6$
Electron Mobility (cm^2/V-s)	1420	2000
Hole Mobility (cm^2/V-s)	470	1800
Electron Saturation Velocity (cm/s)	1×10^7	$1.5 - 2 \times 10^7$
Hole Saturation Velocity (cm/s)	9×10^6	1.05×10^7
Neutron Transmutation cross section (mb)	80	3.2
Energy to Create electron-hole pair (eV)	3.6	13-16

Trace materials can be added to dope diamond so that it performs as a semiconductor. This option has long been used in the electronics industry in microwave applications [3].

Diamond's highly ordered, highly stable structure is at the root of its usefulness in terrestrial electronics. Some of the resulting properties, however, may restrict its use in space applications. NASA GSFC's Advanced Interconnect (AI) program is considering the advantages and limitations of using CVD diamond films and plates in electronic packaging applications that

will fly in space.

Thermal conductivity in diamond is by phonon transmission, as opposed to electron transmission as in metals. At ordinary terrestrial temperatures, phonon movement through diamond is rapid due to the lack of scattering centers. At cryogenic temperatures, however, phonon scattering increases, drastically reducing thermal conductivity [4].

Diamond's electrical, thermal, and optical performance stability in radiation environments is also better at higher temperatures. Diamond and graphite behave similarly in radiation, with diamond showing degradation to a greater extent than graphite. The changes in the performance of the material are mainly due to shifts in the lattice spacing, which causes the material to have lower density. This lower density has negative effects on the hardness and has been found to cause a rise in the internal energy [13]. Annealing has been observed at temperatures above 400°C [(14)].

There is a potential problem at high temperatures also. CVD diamond film can withstand very high temperatures (<800°C) without damage; however, in the presence of atomic oxygen, it can transform to graphite at 625°C [(4)].

Diamond's high electrical resistivity creates a potential problem in high radiation environments. It will not be usable in space if deeply penetrating charged particles cannot be properly drained, as low drainage could result in a destructive electrostatic discharge. Testing is being planned to measure the net amount of charge accumulated, the conditions for discharging, and the results of discharging in CVD diamond when it is exposed to a source of charged particles. Figure 5 is a drawing of the proposed test set-up.
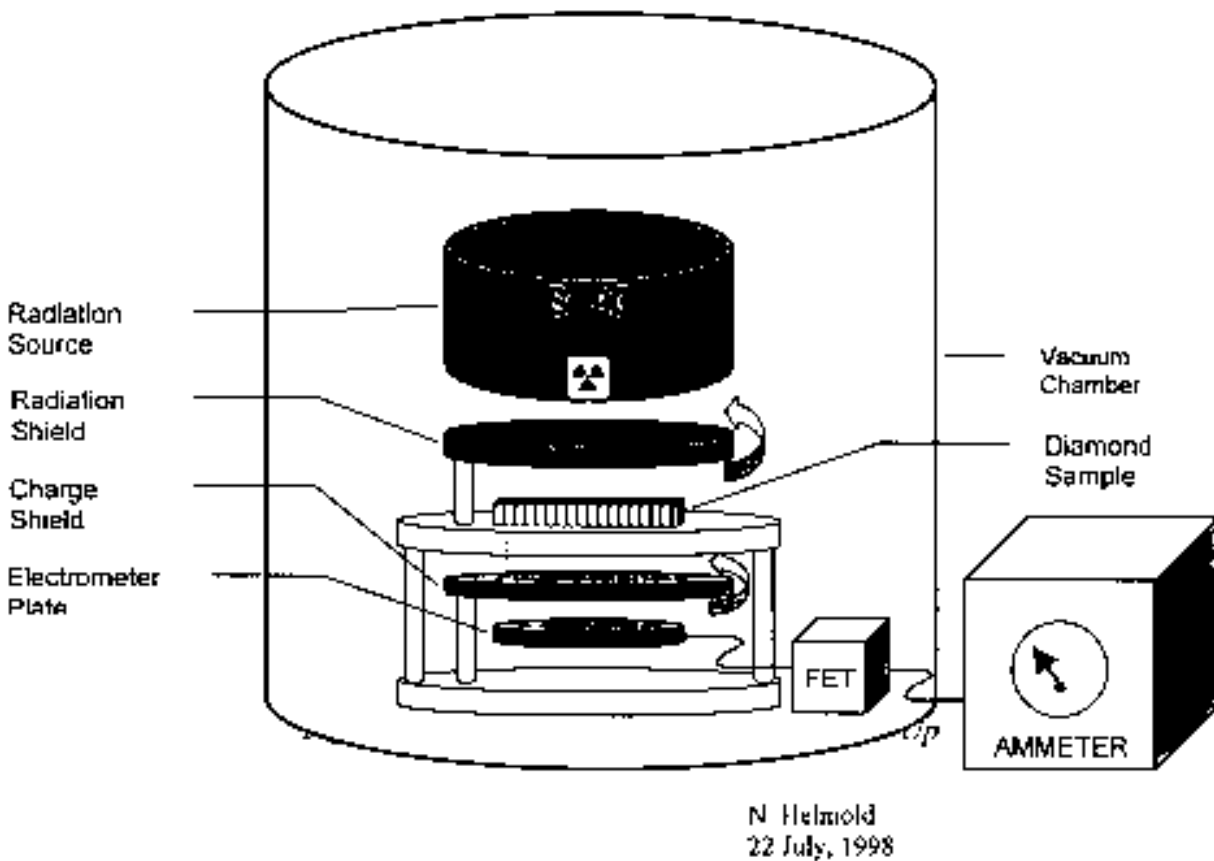

Figure 5. Deep Dielectric Charging Test Set-Up

The AI program will also investigate the cost for small (< 100) quantities of metallized diamond substrates, metallized ceramic substrates with diamond film on one side, and diamond plates with laser cut features. This will help to define the types of NASA programs and electronic packaging designs that can take advantage of this material.

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