Executive Summary
CVD Diamond Film Project
WPI Major Qualifying Project

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October 13, 1999

Introduction

The excellent mechanical, electrical, and thermal properties of diamond are crucially important to a number of industries and have opened advancement in a number of areas, such as electronics. Diamond has the highest thermal conductivity of any known material, and is an extremely strong material due to the carbon bonds in its crystalline structure. The combination of these outstanding properties make diamond exceptionally valuable.

Commercially grown diamond has recently become economically usable in industry. The most common method of diamond film growth is chemical vapor deposition (CVD). This technique produces synthetic diamond on a substrate, and this diamond holds many of the same valuable properties as natural diamond, although not always to the same exceptional extent. The rate at which diamond film is grown has been increased, and therefore the cost of synthetic diamond has lowered considerably.

Lasers have become an important factor in dealing with diamond films since they are one of the few tools that can cut through diamond. The Nd:YAG laser has become a popular choice for CVD diamond cutting. Given the correct parameters, a clean cut can be made without the diamond film cracking.

Although diamond has many characteristics that are beneficial in the electronics field, it is very difficult to work with. One major difficulty is the inability of metal to form a strong bond with the diamond surface. In particular the lack of dangling carbon atoms on the surface of the diamond film makes it difficult for metals to form a strong metal-carbide (Me-C) bond. Although many techniques used for metallizing diamond have been proposed, with varying ranges of success, the most widely used techniques include vacuum evaporation, plating and sputtering.

Project Statement

This project was conducted at the National Air and Space Administration (NASA) Goddard Space and Flight Center (GSFC). The goal of the project was to determine what can be done with diamond in the facilities located on site. Goddard projects normally send diamond films off-site for processing. Unfortunately, this is a costly and slow process that could be greatly reduced if processing could be done on site.

The diamond purchased for this research project consisted of one-inch squares of diamond film, 0.01 inches thick. These diamond films were unpolished, with an approximate roughness of 25 microns. Twenty-six samples were characterized, cut or metallized, and analyzed.

Results – Laser Cutting

The need to shape diamond pieces, for both testing and other applications, lead to the search for possible methods of cutting diamond films at GSFC. The Nd:YAG laser (8=1064 nm), located in building five, was chosen as the most probable cutting tool for diamond because of the laser properties it exhibits, as well as its computer-controlled X-Y translation table. Conveniently, the Nd:YAG laser is, quite possibly, the most popular type of laser used to cut diamond film in industry.

The Nd:YAG laser cuts the diamond film by heating a pin-point sized area of the diamond surface sufficiently enough to break the C-C bond. This results in a thin, precise cut into the diamond. However, there are complications with using the laser. The most critical problem is that the diamond film is transparent at the wavelength used. This is typically avoided by pulsing the laser and allowing it to concentrate its energy on the graphite created from the last pulse by freeing the carbon atoms during the previous pulse. The first laser pulse creates graphite before cutting can begin.

The laser, operated by Mark Mann, is a Q-switched Nd:YAG laser built by Lasag Industrial Lasers, model KLS 322. It was purchased for welding purposes, which meant that the laser's maximum frequency was lower than what is frequently used to cut diamond film in industry. The maximum theoretical frequency, or the number of pulses per second, for this laser is 300 Hz, whereas lasers that cut diamond film in industry normally operate over 1000 Hz. Despite this significant difference, the research demonstrated that this laser will indeed cut diamond film.

Due to the cost of diamond film, an exhaustive series of tests using the laser to cut the diamond film was not practical. Instead, research was completed to find which cutting parameters were the most influential. Laser frequency, table feed rate, and laser power appeared to be the most critical parameters, and were thus closely controlled and adapted to improve the process as the cutting trials progressed. *Figure 1* shows a flow chart that explains the strategy used to cut the diamond and make appropriate parameter changes. Each parameter is briefly described below in the bulleted list.

- The support surface, or substrate, was the first parameter investigated during our experiments. Air, glass slides, and silicon wafers were all used as substrates at various times during the experimenting process. The choice of substrate was important because heat dissipation is important when thermally cutting something as brittle as diamond film.

- Laser frequency was the next factor considered and began with settings in the range of 20-40 Hz before finding a more appropriate range between 225-275 Hz.

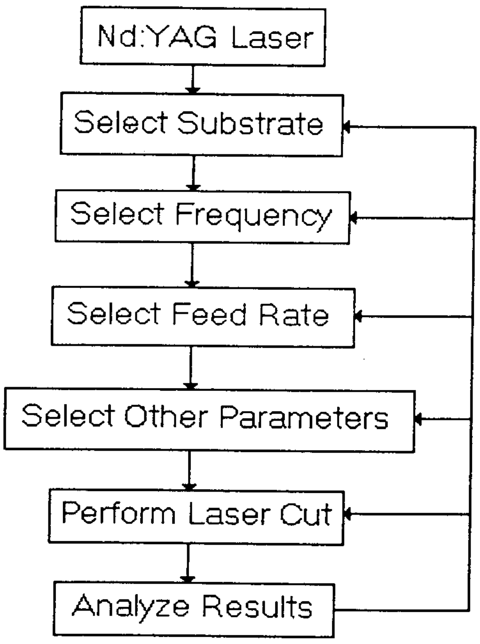

Figure 1: Evaluation and cutting process flow chart

- The feed rate was continually changed based on the visual observations of the last cut. If the cutting appeared too intense, the feed rate was increased to lessen the time the laser was allowed to cut. If very little cutting happened, the feed rate was typically decreased to increase the laser cutting time.

- Other parameters were also modified including the pulse frequency, O_2 flow, voltage, and surface condition (bare diamond film, tape covered, and graphite paint). Bare film would allow the laser to directly cut the diamond. The tape-covered option is merely cosmetic, as its purpose is to allow the graphite residue to settle on the tape and not the diamond for easier cleaning. The graphite paint is used to provide added graphite for the laser to focus on.

- Once the results were visually analyzed a decision was made as whether or not to attempt multiple passes at the same settings.

Once a cut was complete, it was studied through visual inspection and the settings were altered to improve the cutting process. This experimental procedure was repeated several times on each diamond film before it was removed from the laser and studied under microscopes.

Thermal cracking was found to be the major complication in the cutting process. Thermal cracking occurred when the diamond film became over heated and cracked, to relieve the thermal expansion stress induced by the laser cutting. These cracks structurally weakened the diamond film when and where they occurred and needed to be eliminated if the cutting process was to be successful. Unfortunately, due to the lack of time, this problem was not completely eliminated, however the only cracking that occurred during cuts at 250 Hz consisted of one crack directly below the trench. This crack would most likely be eliminated when the trench was cut completely through.

It was found that a thin layer of graphite (in paint form) needed to be applied to the surface of the diamond film during cutting experiments, in order for the laser to be able to cut the diamond film at higher laser frequencies. This coating process is inexpensive and easy to apply so it was considered an acceptable process requirement, particularly since the diamond can be easily cleaned in a boiling acid bath to remove any contaminants or graphite completely before further processing is done.

Although further research is still needed to fine tune the laser parameters, the best results were found in the 225-275 Hz range, at an energy level around 0.18 J, and at a table feed rate of 25 mm/min. However, several other parameters need to be fine-tuned, including the energy versus feed rate ratio, to minimize or eliminate thermal cracking. Unfortunately, it is unlikely that this particular laser will be able to effectively cut the diamond on a flight quality part, although for other projects, such as models and electronic testing, it should prove sufficient and become a useful resource.

Results – Diamond Film Metallization

Metals selected for diamond metallization should be chosen based primarily on their specific mechanical and thermal properties. The metals should possess a CTE close to that of diamond and form a strong bond with the diamond, such as a Me-C bond. In addition, for these experiments, metals were chosen based on the conductive and resistive electrical properties desired. To achieve all of these requirements, metals are often used in layers. The first layer typically consists of a metal that bonds well to a diamond film and has a closely matched CTE, while the top layer possesses the desired electrical properties.

To increase the bonding between the diamond and metal interface, the diamond surface was first cleaned. The first step in cleaning the sample was to remove general contaminates, such as oil and dust, from the film surface. The second step in cleaning the diamond was to prepare the surface for bonding. An argon ion bombardment method was used for the purpose of this project.

A process to metallize the diamond was determined through research of the GSFC facilities. The two accessible metallization techniques were vacuum evaporation, operated by George Harris and plating, operated by Charles Adams. Both processes limited the type of metals that could be metallized onto the diamond. Resistance evaporation was chosen as the primary method of metallizing the diamond film. Due to the preparation procedure, which was less intensive than that of plating, metallization was successful in demonstrating both of these techniques.

Once metallized, it was necessary to test the adhesion strength and stability of the bond between the diamond and the different layers of metal. There are a number of tests capable of measuring the strength of the bonds, all of which range in accuracy. Some tests that were available include: tape test, scratch test, pull test, thermal cycling, and vibration test. These tests were chosen to measure the bond strengths under various conditions using the military standard 883 for thermal cycling and military standard 202 for vibration testing.

As shown in *Table 1*, a number of diamond films were metallized, each with a target thickness to maximize the bond strength. Sample 1 was the first diamond film to be metallized by resistance evaporation within a vacuum chamber. The chrome layer was deposited at a rate of 4 Å/s, while the ensuing gold layer was deposited at a rate of 30 Å/s. Samples 4, 5, 6, 7, 9, 13, 14, and 15 were all deposited at the same rate, and used the same metallization process as the first sample. The only variation in the samples was the thickness of metal deposited on each.

Sample	1st Layer	Target Thickness	2nd Layer	Target Thickness	Metallization Date
		(angstroms)		(angstroms)	
1	Cr	125	Au	1200	8/18/99
4	Cr	250	Au	1200	9/17/99
5	Cr	500			9/17/99
6	Cr	250	Au	1200	9/17/99
7	Cr	250	Au	1200	9/17/99
8	Cr	250	Au	1200	9/17/99
10	NiCr	250	SiO_x	1000	9/24/99
13	Cr	250	Au	1200	9/23/99
14	Cr	250	Au	1200	9/23/99

Table 1: Target thickness for diamond samples metallized by resistance evaporation

Post metallization proved that the actual thickness achieved for each layer was only a few angstroms off from the desired target thickness. The actual thickness of each layer was determined by the deposition rate monitor, located in the vacuum chamber itself.

Sample 8 was the only diamond film that was first metallized using resistance evaporation, then by electroplating. An initial layer of Cr, then Au was deposited by resistance evaporation on the film sample, so the film was able to conduct the current required to plate the sample. The diamond was then plated with a layer of electroless nickel, followed by a top layer of gold.

Since diamond applications are being considered for the GSFC Nanosat program, it was important that the metallized diamond be able to withstand the changing environments it may experience during take-off and throughout its operation time in space. As a result, tests were chosen on the basis that they would contribute to the development of diamond applications for the Nanosat program, as well as limiting testing techniques to the equipment available on-site at GSFC.

The strength of the bond between the diamond and the metal, as well as between the two metal layers, was tested in various ways. Tests that measured the actual bond strength of the metallization were the tape test and the pull test. The tape test used 3M Scotch Masking Tape number 250, which was pulled perpendicular to the metallized film surface. The Instron 4400R, operated by Michael Viens, was used as a testing devise for the pull test. The fixturing and the direction of the load are noted in *Figure 2*. The results from both the tape and pull tests are noted in *Table 2*.

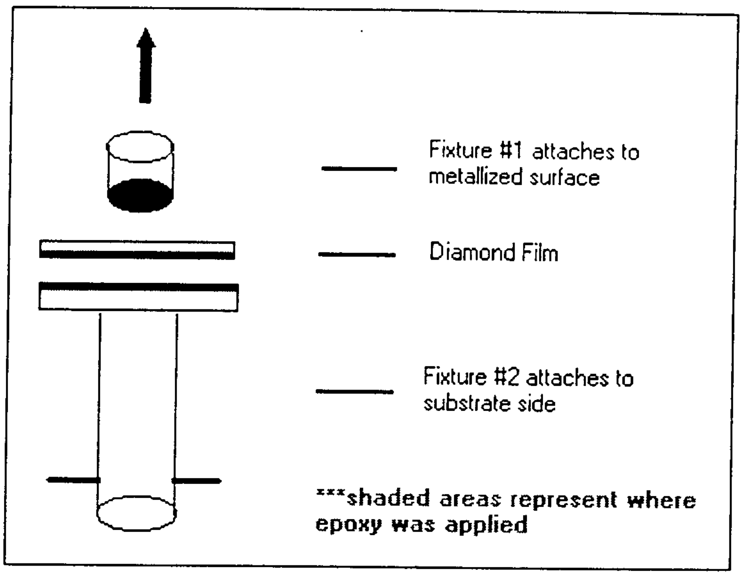

Figure 2: Schematic of pull test

Sample	Tape Test	Pull Test	Failure
		(psi)	
1	nc*	2694.2	gold/chrome
4	nc	2711.0	epoxy
5	nc	2264.3	chrome/diamond
6	nc	6025.0	diamond
7	nc	3864.0	diamond
8	nc	1018.0	mult. Metal layers
10	nc	4995.9	epoxy
13	nc	4194.8	epoxy
14	nc		
15	nc		

Table 2: Results from tape and pull tests
** Denotes no change in the metallization layer*

Thermal cycling was also performed to test the bond strengths after exposing the metallized films to extreme temperature conditions. Samples 6 and 15 were the two Cr/Au metallized films that were tested. Both the Delta 9023 and Delta 9039B were used to test the samples. Thermal cycling temperatures ranged from -65 ^{0}C to 150 ^{0}C for 10 cycles, with a dwell time of 10 minutes at each of the extreme temperatures. There was no visible reduction in metallization bond strengths after thermal cycling was conducted.

Sample 13 underwent a vibration test to determine if the metallization bond strength deteriorated under high frequency conditions. Testing was completed on the BW-100 vibrator, operated by Hennings Leidecker. The vibration test included 12 sweeps that ranged from a lower limit of 5 Hz to an upper limit of 5000 Hz. The three planes of the diamond sample, x, y, and z, underwent the 12 sweeps at the specified frequencies. The vibration test showed no visual damage to the metallization layers.

A combination of the testing methods allowed for a determination of what factors decreased or did not effect the bond strength between the metal and the diamond, as well as between the two metal layers. *Figure 3* is a flow chart to highlight the strategy behind the testing organization.

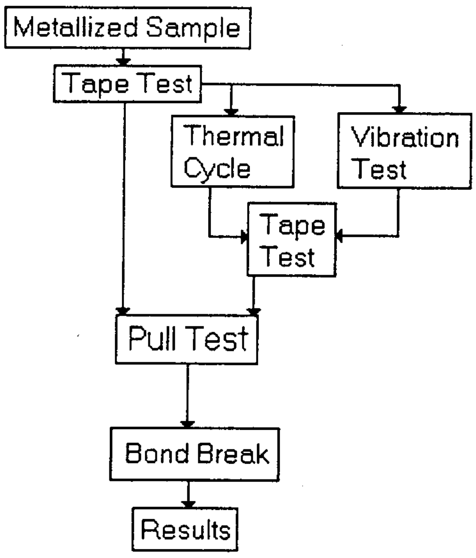

Figure 3: Flow chart of testing procedure

From the results of a combination of all testing methods, it was determined that resistance evaporation is a reliable and manageable metallization process. In pull testing some of the samples, the epoxy failed before the diamond to metal or metal to metal bonds failed. In two instances, the diamond actually broke before the epoxy or the bonds failed. It was also observed that exposing the metallized samples to extreme temperature changes and vibrations, the metal-carbide bond was not weakened, nor was the metal-metal bond. In conclusion, the strength testing proved that the metal-carbide bonds were much greater than originally expected.

Results – Resistor Metallization

Along with metallizing the diamond samples and testing the bond strength, diamond was researched as a possible substrate for resistors. The resistors were created on the diamond film through resistance evaporation. The pattern of the resistors was applied using a two step mask system. *Figure 4* shows the parameters of each of the masks, along with the final product of the two.

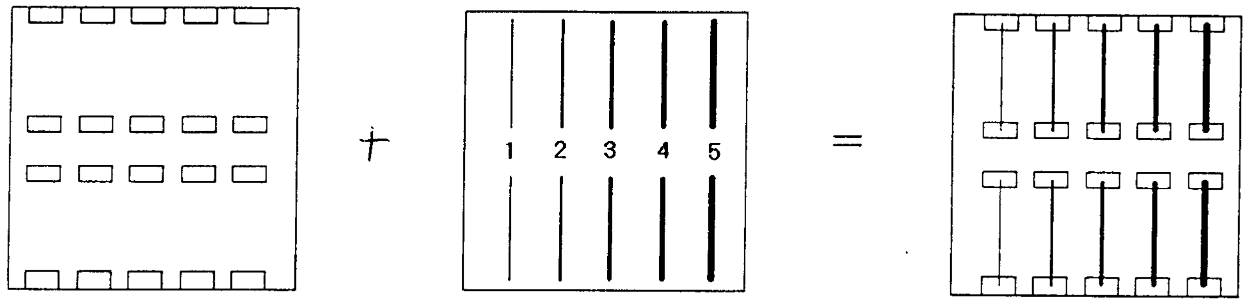

Figure 4: Masks used for resistors

The first mask was used to apply gold bond pads at the end of where each resistor would lie, so that the resistance could be measured. The gold bond pads were evaporated using the chrome/gold layering system, 256 Å Cr and 1206Å Au. The second mask was used to create the resistors themselves. The resistors were made out of nichrome, because of the resistive properties of the material. Silicon dioxide was used as a protective layer to protect the nichrome from oxidizing. The nichrome and the silicon dioxide were both resistively evaporated, 250 Å NiCr and 1010 Å SiO_X.

The nichrome resistors adhered well to the surface of the diamond, and created a successful resistance. The calculated resistance held values of 200 to 400 ohms, whereas the actual resistance measured was ten times that value. There were a few factors that resulted in deviations from the actual values calculated for the resistors. One of which was the rough surface of the diamond film. The rough surface resulted in an uneven coating of the diamond, which could contribute to the divergence from the calculated resistor values. Oxidation of the nichrome was also a possible problem for the variation of the resistor values. The masks used to create the pattern of the resistors were simple aluminum masks, and could be improved, allowing for more accurate patterns on the diamond film surface.

In conclusion, processes have been developed for the cutting, metallizing, and inspection methods of diamond film processing at GSFC. The Nd:YAG laser has the ability to cut through diamond film samples, though parameters still need to be fine-tuned before a cleaner cut can be achieved. Resistance evaporation was proved to be a reliable and manageable method of metallizing CVD diamond film. Under various environments, metallization bond strengths appear unchanged. Resistor development on diamond film has established resistors as a feasible option, although processing techniques need to be modified to obtain a more accurate resistor value. The goal of this project, to locate and develop procedures at GSFC for diamond processing, has been reached.