Proposal for Crystalline Diamond Coatings Utilized in Extreme Environment Window Applications

Emma Griffiths

Department of Materials Science and Engineering

Massachusetts Institute of Technology

May 12, 2020

Specific Aims

The objective of this project is to understand if chemical vapor deposited (CVD) crystalline diamond coatings improve the wear resistance and lifespan of windows in extreme environments, specifically that of Mars.

In order to bring people and equipment to foreign and extreme environments, such as Mars, it is crucial to have high confidence in the performance of the materials used. Maintaining the transparency and mechanical properties of windows are of particular importance, as spacecraft windows are crucial when it comes to carrying out landing, entry, and extravehicular operations. Advanced coatings may be one way to further the lifetime of materials in extreme environments. In order for a window coating to be successful on Mars, it must be able to withstand: low ambient temperatures, thermal cycling, cosmic radiation, dust storm erosion, and high velocity winds. In addition, it must have high mechanical strength, have high adhesion strength with its substrate, and be optically transparent. Window coatings can be developed by varying properties of CVD crystalline diamond coatings.

This hypothesis may be tested by following these specific aims.
1. The **microstructure** of the diamond film can be altered by varying crystallite size (micro/nano). It has been shown that grain boundaries impact the damage pattern of the coating/substrate complex. Varying the crystallite sizes could lead to variations in erosion resistance for this reason. An ideal crystallite size distribution can be determined to maximize erosion resistance without sacrificing coating performance in other areas.
2. The diamond **coating thickness** can likewise be altered via CVD. Thicker coatings may lead to overall improvements in wear resistance. However, coatings too thick may have lower adhesion strength. This can lead to increased average stresses placed on the substrate. Coating thickness can be investigated to find a thickness that maximizes performance without major drawbacks.
3. **Etching** of the substrate can be done prior to coating application. Etching is used on various substrates to improve the adhesion of the coating and can be used to create thicker coats. Should the diamond coating be met with forces above its threshold, the etching pattern may then also affect the extent of coat stripping and delamination. Varying etching patterns can be investigated to determine the optimal pattern.
4. **Interlayers** may be used to bridge the substrate and the coating. CVD diamond has a low thermal expansion coefficient (TEC) and is deposited at relatively high temperatures (around 600°C). This leads to high thermal stress at room temperature as well as intrinsic mechanical stresses. These stresses can cause coating delamination. Substrate/coating thermal expansion coefficient differences can also lead to these failures. An interlayer could help reduce these intrinsic stresses and spread out thermal expansion coefficient mismatch between the substrate and coating. In order for a window coating interlayer to be successful it must also be optically transparent, which poses an additional challenge.

Background and Significance

Spacecraft windows, and the visibility they provide, are crucial in order to carry out landing, entry, and extravehicular operations. No spacecraft coating/window system is yet fully equipped to handle the Martian environment for an indefinite period of time.[1] New window coatings need to be developed in order to ensure that their strength and visibility will not deteriorate over an extended stay on Mars as they withstand new factors such as significant dust erosion.

Currently, NASA creates its spacecraft windows out of layers of aluminosilicate and fused silica glasses. The aluminosilicate glass layers are tempered to maximize their strength. This type of glass usually acts as the innermost layer to act as a barrier between the pressurized spacecraft interior and the low pressure exterior. The fused silica is an attractive choice for the exterior glass layers as it has high optical quality and good thermal shock resistance.[2]

Coatings are also utilized by NASA on these glass layers. The inner glass pane is coated with a red reflector in order to prevent infrared transmission. The central pane and outer pane interior are coated with anti-reflection coatings to improve visible light transmission. The exterior of the outer pane, however, is uncoated.[2] Extended period dust erosion can then leave the windows subject to decreased visibility, cracking, or failure. In order to have a successful mission these must all be avoided.

Various coating materials for extreme environments have been recommended depending on their intended use. Window coatings are particularly limited in material possibilities since they need to be not only strong but also transparent. Crystalline diamond coatings have been suggested for uses when transparency is desired, abrasion and erosion are a concern, and where wear control is desirable.[1] They prove to be a great base candidate for extreme environment window applications.

Prior research has confirmed the potential for crystalline diamond coatings to be successful in this application. It has been shown that a thin diamond layer can provide significant mechanical protection for its substrate. This corresponds with higher terminal particle velocity before crack or failure initiation.[3] Now that the potential for crystalline diamond coatings has been confirmed, a better understanding of how changing CVD processing parameters is needed to optimize the coatings. In literature, there is no conclusive evidence as to how varying CVD processing parameters impacts CVD crystalline diamond coatings and thus their overall effectiveness.

CVD parameters can be altered resulting in various diamond crystallite sizes (micro/nano). Varying crystallite sizes and microstructure can influence crack propagation and damage formation in the coating via changes in grain boundaries. Research has shown that diamond crystallite size can be altered reliably by changing the gas phase chemistry of plasma-enhanced chemical vapor deposition process (PECVD). Traditional CVD methodology involves the use of a CH_4/H_2 precursor and results in diamond films with crystallite sizes ranging from 1-10μm. It

has been proven that hydrogen can be replaced by a noble gas, such as argon, in diamond CVD. Because of high secondary nucleation rates, the addition of the noble gas results in diamond films with crystallite sizes as small as 3-15nm. The noble gas/hydrogen ratio can be altered to create crystalline diamond films of a desired crystallite size distribution.[4]

Varying crystallite size and repeated CVD thin film coats can be used to alter overall coating thickness. Etching can also be done to allow thicker coatings. Etching improves coating adhesion to the substrate by increasing potential bonding surface area. Etching can be done mechanically or chemically. There is no conclusive literature study that investigates varying etching techniques and patterns and their impact on crystalline diamond coating adhesion and uniformity. A high degree of etching may also result in reduced visible light transmittance, so it is possible that an intermittent etching degree will result in optimal coat performance. This research project aims to understand how all of these factors -- crystallite size/microstructure, thickness, and etching technique influence overall coating performance and uniformity and which processing considerations are necessary to produce the optimal coat.

Literature has shown one significant downside regarding the use of CVD crystalline diamond coatings. Thermal expansion coefficient mismatch between substrate and coat leads to higher than desired intrinsic mechanical stresses. It has been shown that this problem is extremely important regarding coating failure.[3] The diamond coatings increase threshold impact velocity for particulates before damage, but because of these intrinsic stresses an impact above threshold velocity can be detrimental. Such an impact can lead to delamination and extensive coating stripping or even sample failure. It is very risky to apply coatings that have such severe consequences should an impact above threshold velocity ever occur (especially since this is not particularly unlikely in a foreign and extreme environment).[3] A proposed solution to this is an interlayer between substrate and coating to help reduce intrinsic stresses.

Interlayers are not an entirely new concept, as layers are commonly used with tempered and laminated glasses to create stronger overall materials. One common use of this practice is car windows and windshields. Car windshields in particular use resins such as polyvinyl butyral (PVB) between laminated glass layers. Car windshield interlayers may prove a good place to begin investigating potential materials for crystalline diamond coat/substrate interlayers since they help improve overall strength and are also transparent. Literature has yet to find an appropriate interlayer to place between the glass substrate and crystalline diamond coating. Furthermore, additional challenges to address when considering interlayers include ensuring they are optically transparent, have some form of adhesion to the substrate as well as the coating, and do not result in a significant coating performance penalty. If this significant drawback of CVD crystalline diamond coatings remains unaddressed, then this type of coating may prove to be unusable despite its promise.

Experimental Outline

Quantifying Performance

In order to understand how varying CVD diamond coating properties impacts overall performance, it is important to have testing procedures that quantify the mechanical, optical, and thermal properties of the coatings. For a window coating application in extreme environments, it is especially important to investigate the erosion resistance, opacity, adhesion strength, surface properties, and the impact of thermal cycling as coating properties are varied. Successful coatings will have higher erosion resistance, lower opacity, higher adhesion strength, smoother surface/higher overall uniformity, and perform consistently. The following experiments will be done to assess the performance of the coating in each area:

1. Erosion Resistance

The erosion resistance of the coating will be quantified via droplet and particulate erosion tests. It is important that the coatings have a high erosion resistance to ensure that they will increase the lifetime of the substrate.

A multiple-impact jet apparatus (MIJA) can be used to simulate the impact of spherical raindrops via a smooth-fronted water jet.[3] MIJA experiments find the absolute damage threshold velocity (ADTV). This is done by impacting the coating/substrate sample repeatedly at a certain velocity and checking for damage via a microscope.[3] If no damage is seen, the velocity is increased and the experiment repeated until signs of damage are displayed. The ADTV is recorded, and a higher ADTV corresponds to a more successful coat. An example micrograph of a sample post erosion test is shown in Figure 1.
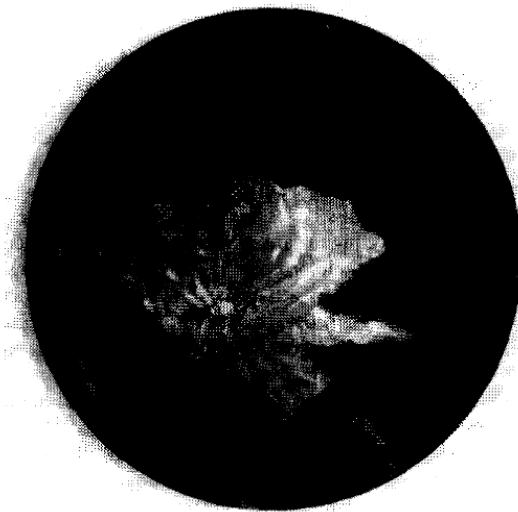
A similar experiment can be done with particulate erosion. Pressurized air can be used to accelerate grains of sand. The extent of erosion can be quantified via a mass loss experiment.[3] More successful coats will have a lower mass loss after the sand erosion, as that would mean less of the coating was stripped from the substrate. The velocity of the particulate can be increased and mass loss performed to find the ADTV (corresponding to when statistically significant mass loss begins to occur).

2. Opacity

The opacity of the substrate/coating complex can be quantified using visible light spectroscopy. This test can measure sample transmittance as light wavelength varies. Successful coatings will be transparent in the visible light range (380-740nm). It is critical that the windows remain clear in the visible light range so that they can continue to be used for necessary operations and inspections. A broader range of wavelengths could also be tested in order to fully quantify coating performance in different sections of the EM spectrum.

3. Adhesion Strength

Nanoindentation can be used to measure the coating adhesion strength with the substrate. It is critical that the coating and substrate have high adhesion. The coating will fail due to poor adhesion even if the coating itself seems to perform well in other areas. A wedge delamination test can be used to estimate coating adhesion.[5] A wedge indenter can be driven through the coating and into the substrate. The substrate plastically deforms due to this force, and this results in coating delamination. The size of the delaminated area can be related to interface toughness and adhesion strength.[5] A smaller delaminated area under the same load conditions will correspond to a sample with higher adhesion strength between its substrate and coating.

The delaminated area can be measured using an optical microscope. How adhesion strength varies across coatings can be understood by comparing coat delaminated area sizes for the same test load conditions. The same baseline coating will be used for all adhesion tests so that adhesion strength can be compared across varied coating parameters. The baseline coating used will be 2µm thick, CVD-deposited microcrystalline (average crystallite size of 10µm) diamond on a fused silica glass substrate. The glass substrate will be unetched and there will be no interlayer. A nanoindentation test on this baseline sample will be performed, and 1/(delaminated area) will be used to approximate the adhesion strength dependence. Each following nanoindentation test with varying coat parameters will be compared relative to this baseline using its measured delaminated area. Comparing the properties of the new sample to that of the baseline will provide insight as to how changing that coat property impacted its adhesion strength.

4. Surface Smoothness and Coating Uniformity

It is important to investigate coating surface properties to understand whether there is a trade off between erosion resistance and surface smoothness. For example, it is hypothesized that coatings composed of nanocrystalline diamond will have a smoother surface than that of microcrystalline diamond, but due to variations in grain boundary structure and a decrease in phase purity, nanocrystalline diamond could lead to reduced erosion resistance. Investigating smoothness, uniformity, and grain structure as numerous coating parameters are varied can confirm whether or not such a trade off in coat performance exists.

To analyze the samples's surface, scanning electron microscopy (SEM) will first be used. SEM can provide a visual of surface morphology and nucleation density after the films have been grown. Atomic force microscopy (AFM) will then be used to more closely inspect surface topography. To specifically analyze the grain boundaries of the different crystallites and their respective orientation, electron backscattering diffraction (EBSD) will be used. EBSD is usually performed by looking at the film/substrate interface. In order to do this, the substrate is removed to reveal the surface of the bottom of the film. EBSD uses a focused incident electron beam to map the diffraction pattern of the top 200-500nm of the sample.[7] This can be used to determine the crystallites' orientation and the location of the grain boundaries. From this information, the film texture can be mapped. The inspected surface may require additional polishing to prepare for the EBSD process. Ion milling can work as the polishing method.[7]

It is also possible to use EBSD to create a 3D recreation of the film's grain structure. This is done by performing an EBSD measurement, ion milling the top layer of the film, and repeating the measurement to build up the grain structure.[7] For the purposes of this experiment, EBSD will primarily be used just to map the 2D grain structure of the first layer of the film. Depending on the outcome of the results, mapping additional layers to better understand 3D grain structure might become necessary to better understand failure patterns and mechanisms, especially for thicker coats.

There is some overlap in the measurement capabilities of each of these measurement techniques. Depending on the results and whether or not each test provides necessary and helpful information, the number of techniques used may be reduced.

5. Thermal Cycling

Materials in extreme environments undergo significant temperature variations. Since coatings and their respective substrates likely vary in thermal expansion coefficients, significant variations in temperatures can exacerbate intrinsic stresses and result in failure. Temperatures

on Mars specifically vary from -140ºC to 30ºC.[6] It is not completely understood whether significant delamination will occur spontaneously due to temperature variations alone or whether temperature variation needs to be coupled with a particulate/droplet impact. Because of this, a series of tests will be performed to better understand how changing temperature impacts performance.

First, the sample will undergo a thermal cycle test. The sample will be cycled 100 times between -140ºC to 30ºC to replicate the Martian climate. One cycle corresponds to the sample being held at -140ºC for 30 minutes and 30ºC for 30 minutes. If significant delamination is seen after this test, then the sample will be automatically considered a failed composition. If not, two fresh samples (that have not been thermally cycled) of the same composition will be used in a variation of the erosion tests described above. Each of the samples will undergo the same erosion tests, but one will be held at -140ºC while the other is held at 30ºC. If significant delamination occurs in either sample prior to reaching the ADTV measured at room temperature, then it will be clear that the delamination was a result of the temperature variation coupled with an impact. Coating success will be rated based on the degree to which the measured altered-temperature erosion test ADTV values vary from that of the room temperature values. More successful compositions will have a smaller percent difference between their room temperature and altered temperature measured ADTV values. In an ideal case, the composition will perform consistently despite the temperature it is held at.

There are many other permutations of this experiment. For example, the samples could be thermally cycled, and then the same sample could be used for a room temperature erosion test. Previously thermally cycled samples could also be used for the altered temperature erosion test rather than fresh samples. Depending on the outcome of the proposed experimental plan for thermal testing, these other permutations may become more necessary to explore.

Quantifying Performance Summary

The above experiments can be performed to quantify coat performance in the areas most crucial for an extreme environment window application. These experiments will be returned to and repeated as each coat parameter is varied. It is important to note that the baseline coating for all performance experiments will be 2µm thick, CVD-deposited microcrystalline (average crystallite size of 10µm) diamond on a fused silica glass substrate. The glass substrate will be unetched and there will be no interlayer. Each coating parameter change described below will impact only one of these baseline qualites and the others will remain the same. This will provide a direct understanding of the changed parameter's influence on the coating's performance. The exact coating parameters that will be varied and how they will be varied is described in detail below.

Varying Coat Properties

Microstructure

1. The effects of varying the crystalline diamond microstructure can be investigated by controlling crystallite growth size in the CVD process. The coating's microstructure and its relation to overall performance is yet to be understood. It has not been shown that the crystallite size is proportional to performance. Smaller crystals would lead to a smoother coating surface and higher uniformity which is beneficial for coating applications. However, a smaller crystallite size also leads to a higher carbon percentage at the grain boundaries. For example, 300nm crystallites correspond to about a 0.1% carbon fraction at the grain boundaries, while 3nm crystallites correspond to a carbon fraction of about 10%.[4] Because increased carbon fraction at the grain boundaries decreases phase purity throughout the coating, this can have a significant impact on the coating's properties. For example, smaller crystallites and a correspondingly lower phase purity can result in lower overall fracture toughness.[4] Because smaller size increases smoothness but decreases phase purity, it is likely that there is a diamond crystallite size distribution that leads to optimal coating performance and maximizes this trade off.

Crystallite size can be controlled reproducibly by altering the gas-phase precursor chemistry in the CVD process. A fused silica glass substrate can be used to replicate the exterior glass panels of NASA's spacecraft. Typical CVD requires a CH_4/H_2 precursor. Altering these gas ratios and the addition of argon allows controlled crystallite size variation.[4] The results of this process and the gas ratios corresponding to various size distributions are confirmed in Figure 2.

High-resolution scanning electron microscopy (HREM) can be used to determine and confirm the actual crystallite size distribution. The {111} lattice planes are the easiest to see with available microscopy techniques. An HREM image of the film can be taken so that the crystallites have their {111} planes parallel to the imaging incident electron beam. This allows for the visualization of individual crystallites via altering {111} directions and sharp lattice fringes.[4] An example HREM image as described is shown in Figure 3. A crystallite size distribution can be determined by analyzing the HREM image. Crystallite size can be approximated by taking the largest dimension across the crystallite area where {111} lattice fringes are visible.[4] Repeating this process on numerous crystallites can be done to produce an approximate crystallite size distribution for the film. Knowing the crystallite size distribution for the coating will allow a better understanding of how size impacts coat performance. This can lead to the determination of whether or not there is a certain size distribution that leads to optimal coating performance.

Given this information, it is possible to deposit and test crystalline diamond films ranging in average crystallite size from ~3nm to ~10µm by varying precursor gas rations in CVD. This range of crystallite sizes will be deposited on a fused silica glass substrate to best replicate the exterior glass panels of NASA's spacecraft windows. Larger crystallite sizes (~10µm) can be achieved with a CVD precursor gas ratio of 1% CH_4 to 99% H_2. Smaller crystallite sizes require the replacement of H_2 with argon gas. The smallest sizes (~3nm) require complete replacement (1% CH_4 to 99% argon). The precursor gas ratio will start at 1% CH_4 to 99% H_2. The film will be deposited via CVD and then characterized using HREM. The film will then be tested for performance as specified in the first section. The H_2 will then be replaced in 10% intervals by argon gas and the characterization and performance tests will be repeated until all of the H_2 is replaced by argon. It will then be possible to see if a certain average crystallite size led to an optimal coating performance.
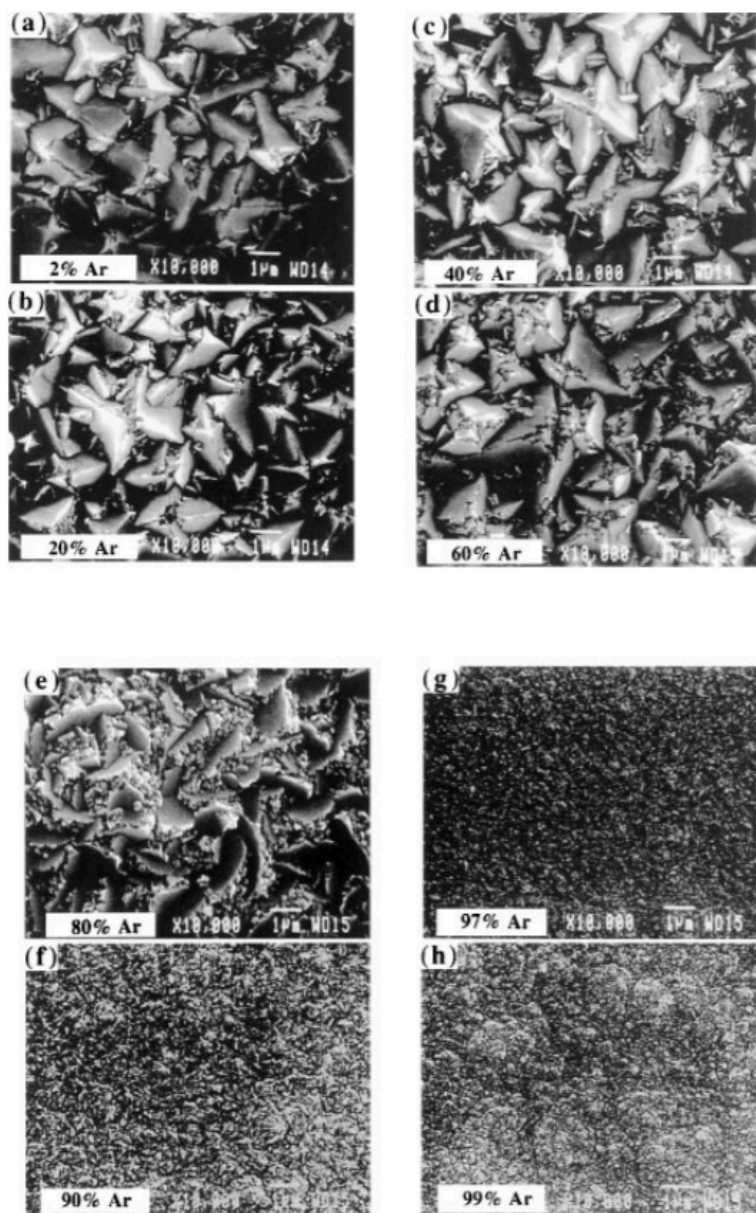
Figure 2   SEM images of crystalline diamond films grown from microwave plasmas. The CH_4 percentage in the gas phase precursor was held at 1% while the ratios of Ar and H_2 varied. The images show a transition from microcrystallinity to nanocrystallinity and their corresponding precursor gas mix ratio.[4]
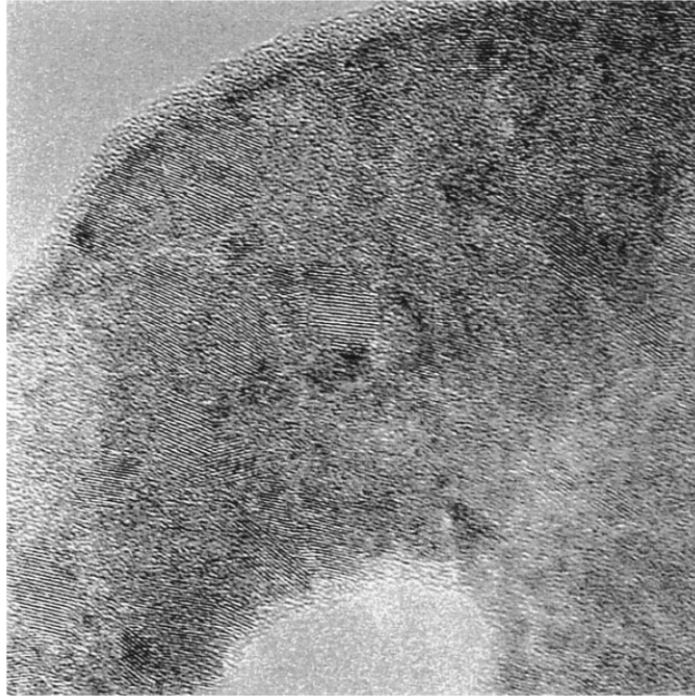
Figure 3   HREM image with diamond crystallite that have their {111} planes parallel to the imaging incident electron beam. {111} lattice fringes are visible and can be used to determine the crystallite sizes and their distribution. The average crystallite size was between 3-5nm.[4]

Coating Thickness

2. Like the microstructure, the coat thickness can be altered during CVD. Thicker coatings are predicted to improve wear resistance, but may also result in decreased adhesion strength with the substrate and have higher intrinsic stresses.

CVD, if performed as described in the previous section, will lead to the nucleation of randomly oriented diamond crystallites. It has been shown that using a voltage bias (imposed on the substrate) during the process leads to a preferred crystallite orientation as well as an enhanced nucleation process.[7] This biased enhanced nucleation (BEN) process may be necessary to generate thicker films. Growth rate can be carried out at approximately 0.5-1µm per hour. The film thickness can be confirmed by performing a mass loss experiment. Thicknesses 5-10µm will first be investigated (increasing thickness in 1µm intervals). This range may be expanded or reduced depending on the preliminary results. The procedures for quantifying performance will be repeated to understand how thickness influences performance and to see if the relationship is as hypothesized. These results will also be used to adjust the thickness range as needed.

Etching

3. Etching of the substrate prior to CVD deposition has been shown to improve coat adhesion and allow the deposition of thicker layers. However, it is not conclusively known whether there is a preferred etching method/depth for crystalline diamond coatings deposited on fused silica or how etching patterns may influence or minimize failure.

The primary etchant to be used is buffered hydrofluoric acid (HF). This etchant is commonly used on fused silica glass. The etching process and rate can be altered by changing etching conditions. The concentration of HF dissolved in water can be altered. Higher HF concentrations will lead to a higher etch rate and a higher degree of etching. The etch bath temperature can also be altered, as higher temperatures will increase the speed of the chemical reaction and thus the degree of etching.[8] For the purposes of this experiment, HF concentrations will be held constant at 48% dissolved in H_2O (commercially available). The etch bath temperature will be varied from 25-45°C in 5°C intervals. Etching will be done for 2 hours.[8] Each variation of etchant concentration and temperature on the fused silica substrate will be followed by CVD crystalline diamond deposition. Performance will be quantified as described above to determine the optimal degree of etching, and ranges and duration may be adjusted depending on the results.

Etching patterns will also be investigated. It has been shown that when the coating fails, it may be removed in discrete areas that follow the underlying etching pattern.[3] Strategically choosing an etching pattern may then lead to a prolonged lifetime. The etching pattern that will be investigated is a standard mothseye structure (columns and valleys).[4] The mothseye nanostructures were initially inspired by the corneal surface of the moth eye. The structure of the surface has an antireflective function which has previously been used to enhance solar cell efficiency and display visibility.[9] Generating these structures on the fused silica substrate involves first using electron-beam or interference lithography to define the desired pattern in a polymer film on top of the substrate. Electron-beam lithography allows for precise control over spacing and arrangement. The pattern is left behind as an array of dots. Mothseye patterns usually consist of columns about 250nm high spaced about 200-250nm apart in an array.[10] To achieve these columns and valleys, CHF_3 mixtures are used to etch the silica substrate.[10] Figure 4 shows an example of a mothseye structure from nature. The performance assessment experiments will be repeated to determine the impact of a defined etching structure.
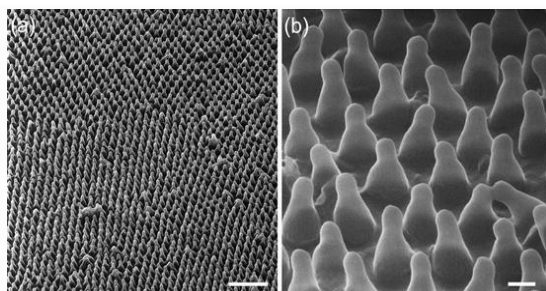

Figure 4   A natural mothseye structure found on the wing of the *Cephonodes hylas* taken via a scanning helium ion microscope. (Scale bars: (a) 1 μm, (b) 100 nm.)[10]

Interlayers

4. Variations in thermal expansion coefficient between the fused silica substrate and the CVD deposited crystalline diamond coating can lead to intrinsic stresses. Interlayers that bridge the substrate and coating may be able to minimize these stresses. Interlayers to be used for window applications may prove to be particularly difficult to determine, as there is an increased challenge of finding a suitable interlayer that is also optically transparent. Because of these challenges, the initial interlayers to be tested will be modeled after those used in the structural design of aircraft windshields and windows. These interlayer materials are: plasticized polyvinyl butyral, polyurethane, and silicone.[11] Since CVD is performed at low pressure, often ranging from a few millitorr to a few torr, it is possible that these interlayer choices may lead to outgassing and difficult coat deposition. Because of this, glass interlayers will be tested as well. Ultra low expansion glass (ULE) as made available by Corning Incorporated will be tested as a possible interlayer. The glass is primarily silica with some titanium dioxide (less than 10%). It is a good candidate for space applications because of its high resistivity to thermal shock. Each interlayer candidate will be tested for performance as described in the previous section. The search for interlayers may be expanded to other materials if the results require it.

Fused silica in particular has a low thermal expansion coefficient of $5*10^{-7}$ $^{\circ}C^{-1}$. The thermal expansion coefficient of diamond is $0.8*10^{-6}$ $^{\circ}C^{-1}$.[12] Since this specific choice of substrate does not have a TEC drastically different than that of diamond, significant inherent failure can hopefully be avoided. Materials like ULE that are designed to have great thermal shock resistance will match even closer in TEC to that of diamond and will likely minimize intrinsic stresses even further. Whether or not interlayers provide significant benefit to samples with a fused silica glass substrate will need to be investigated. Furthermore, if CVD diamond coatings were to be used in more generalized applications, the substrates would vary, and having background knowledge of interlayer possibilities will provide a starting place for this versatility.

Conclusion

In conclusion, the intention of this proposal is to determine if CVD crystalline diamond coatings improve the wear resistance and lifespan of windows in extreme environment applications, such as for an indefinite stay on Mars. The experimental plan in this proposal will also result in the determination of the coating parameters that lead to optimal performance as defined by higher erosion resistance, lower opacity, higher adhesion strength, smoother surface/higher overall uniformity, and consistent performance under temperature variations.

To summarize the results of varying all of these coating parameters, cutoffs for success have been determined. Opacity and thermal cycling have been divided into pass/fail regimes. For opacity, successful samples must have at least 70% transmittance in the visible light range before and after performing the erosion tests. For thermal cycling, successful samples must first show no failure after 100 thermal cycles between -140°C and 30°C. Furthermore, the samples must have a similar ADTV at room temperature, -140°C, and 30°C for the erosion experiments

to be considered successful. The remaining samples will be plotted based on their measured adhesion strength and erosion resistance as shown in Figure 5. Erosion resistance will be plotted based on the room temperature ADTV. Success will correspond to an ADTV over 50 m/s with an average erosive particulate size of 10µm. This is to represent the Martial sandstorms while including a small margin of safety. The adhesion strength will be plotted as the inverse of the measured delaminated area, normalized by the delaminated area of the baseline sample. Success will correspond to an adhesion strength greater than that of the baseline sample. Additional sample fabrication will be done to test a combination of successful sample parameters in hopes of creating a coating that has optimal performance.
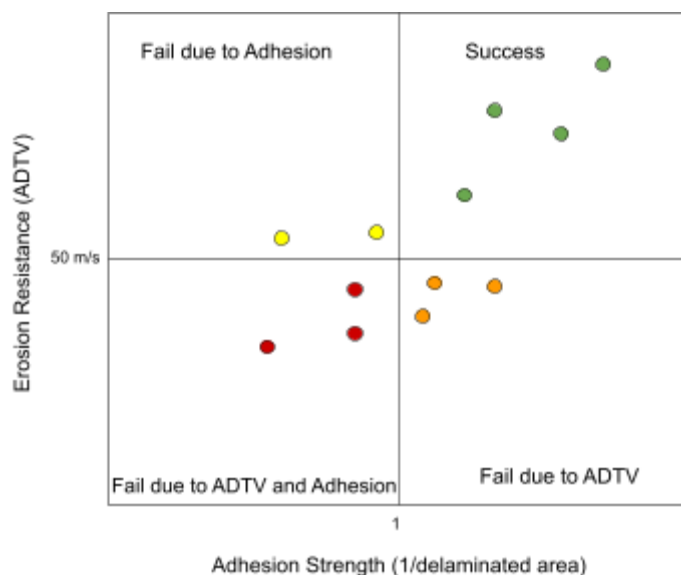
Figure 5   A representation of a success plot that will be made once all data has been collected. Samples that meet the opacity and thermal cycling criteria will be plotted. Successful samples will be in the top right quadrant and their parameters will be used to develop an optimal coat.

Dangers and Safety

It is important to note the dangers associated with performing this experiment in order to ensure proper safety is utilized.

Dust
The particulate erosion tests will involve the use of dirt. This dirt will be accelerated through the air and can create dust clouds. These are very dangerous to breathe. It is important to perform this experiment in an area with proper ventilation or even in a fume hood to minimize exposure to the dust cloud. Powers are also potential explosive hazards and will need to be kept away from ignition sources.

Gas Storage

Performing CVD requires the usage of various gases. These are frequently stored in high pressured gas cylinders. It is extremely important that these cylinders are stored properly, for if they fall the valve may shear and the high pressure gas can provide a lot of force to propel the tank. Proper storage requires the buckling in and tying down of the tanks.

Liquid Nitrogen

Liquid nitrogen will be utilized in this experiment to reach low temperatures. Liquid nitrogen can rapidly freeze skin tissue and eye fluid. It can also result in cold burns, frostbite, and permanent eye damage by exposure. When working with liquid nitrogen, it is important to be working in a well-ventilated area. Furthermore, safety needs to be practiced when handling liquid nitrogen. Loose-fitting thermally insulated gloves should be used, and the liquid should be handled slowly to minimize splashing.

Hydrofluoric Acid

Hydrofluoric acid (HF) will be utilized in the erosion experiment. HF can deeply penetrate the skin. HF burns can affect deep tissue layers. The reactive fluoride ions can circulate throughout the body and cause multiple organ toxicity, including heart arrhythmias and death, if not treated. All MIT employees must be trained before working with HF. HF should be handled in a fume hood. All laboratories using HF must have unexpired calcium gluconate decontamination gel on hand. For concentrated solutions, gloves that cover the hands, wrists, and forearms should be utilized. Goggles should also be worn. Waste HF should be placed in a chemically compatible container (such as polyethylene or Teflon) and should be clearly marked as hazardous waste.

Experimental Plan

Week	Hours/week	Task Description
1-3	40	Cut fused silica glass substrates to size, CVD deposit samples for microstructure test, use HREM to confirm size distribution
4-6	40	Performance testing on microstructure test samples and analyze data
7-9	40	Adjust crystalline size range as results indicate, synthesize new samples, confirm distribution with HREM
10-12	40	Performance testing on weeks 7-9 samples, analyze data, and confirm microstructure relation to performance
13-15	40	CVD deposit samples for thickness test, use mass loss to confirm thickness
16-18	40	Performance testing on weeks 13-15 samples and analyze data
19-21	40	Adjust thickness range as needed, synthesize new samples, use mass loss to confirm thickness

22-24	40	Performance testing on weeks 19-21 samples, analyze data, and confirm thickness relation to performance
25-27	40	Etch silica glass substrates and CVD film deposition for etching tests
28-30	40	Performance testing on weeks 25-27 samples and analyze data, confirm degree of etching and etching structure relation to performance
31-33	40	Synthesize samples with various interlayers and CVD
34-36	40	Performance testing on weeks 31-33 samples and analyze data
37-38	40	Additional research on interlayers as preliminary results necessitate
39-41	40	Synthesize samples with new additional interlayers and CVD
42-44	40	Performance testing on samples synthesized in weeks 39-41 and analyze data, confirm interlayer relation to performance
45	40	Make success plot to determine trends in how various parameters related to ultimate success
46-48	40	Synthesize samples combining parameters of successful coatings based on results of success plot
49-51	40	Performance testing on optimal coatings synthesized in weeks 46-48
52-53	40	Summarize and present all experimental results

Project Budget

Material	Quantity	Cost
Martian Sand Simulant	1 kg	$20
Liquid Nitrogen	56 L	$254
Argon Gas	14 L	$182
Fused Silica Glass	28 * (100 mm dia, 1.5 mm thick)	$3388
HF	800 mL	$359
CHF_3	One size	$656
ULE	TBD - need Quote	TBD - need Quote
Plasticized Polyvinyl Butyral	100g	$24

Polyurethane	thickness 10 mm, size 150 × 150 mm	$241
Silicone	sheet, thickness 2 mm, size 600 × 600 mm	$400
		Total
		~$5524
Equipment	**Time**	**Cost**
CVD	174 hours	$5220
Nanoindentation	38 hours	$950
SEM	38 hours	$2280
AFM	38 hours	$1140
EBSD	38 hours	$2280
Hot Plate	purchase	$390
HREM	12 hours	$1800
		Total
		~$14060

Citations

1. Miyoshi, Kazuhisa. Solid Lubricants and Coatings for Extreme Environments: State-of-the-Art Survey. *NASA.* **2007**.

2. Dismukes, Kim. Forward Fuselage and Crew Compartment Windows. *NASA*. **2002**.

3. Coad, E.J., et al. Aerospace erosion of diamond and diamond coatings. *Diamond and Related Materials*. **1996**.

4. Gruen, Dieter. NANOCRYSTALLINE DIAMOND FILMS. *Argonne National Laboratory*. **1999**.

5. Vlassak, J.J., et al. A simple technique for measuring the adhesion of brittle films to ductile substrates with application to diamond-coated titanium. *Journal of Materials Research*, 12(7), 1900-1910. **1997**.

6. All about Mars. *NASA Science Mars Exploration Program.*

7. Chen, Hon-Wen, et al. The 3-D structure of polycrystalline diamond film by electron backscattering diffraction (EBSD). *Diamond and Related Materials*, 12(10-11), 1633-1639. **2003**.

8. Grosse, Axel, et al. Deep wet etching of fused silica glass for hollow capillary optical leaky waveguides in microfluidic devices. *Journal of Micromechanics and Microengineering*. **2001**.

9. Ji, Seungmuk, et al. Optimal Moth Eye Nanostructure Array on Transparent Glass Towards Broadband Antireflection. *Applied Materials and Interfaces*. **2013**.

10. Boden, Stuart A, et al. Moth-Eye Antireflective Structures. *Encyclopedia of Nanotechnology*. **2012**.

11. Windows and Windshields. *US Department of Transportation Federal Aviation Administration*. **2003**.

12. Burgemeister, E. A.. *Physica,* B93, 165-179. **1978**.