GEMINI
8-M Telescopes
Project

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Coating Removal Processes for an 8-Meter Mirror

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ABSTRACT

The various methods of removing the reflective and protective coatings from the mirror were investigated. Investigations were undertaken to the point of laboratory testing, but no further. The objective of this study is to determine the most effective method, in terms of safety, time, and effectiveness, for coating removal prior to recoating.

Introduction

This report is a study of the various primary mirror stripping processes, and a discussion of the various pros and cons of each process. The Science Review Meetings for the Gemini Project recommended investigating the feasibility of a low-emissivity durable coating for the primary mirror. The target emissivity for the telescope is 2%. At a maximum the emissivity should be no more than 4% after coating, and should degrade to no more than 5% before recoating.[1]

Exactly what is needed to accomplish this goal? First, keeping the mirror clean between recoatings will help, and using a special coating for the mirror will greatly reduce the emissivity. Frequent recoating will keep the emissivity low and the reflectance high. Between these two required steps is another one; the removal of the old coating from the substrate prior to recoating.

The coating must be removed from the primary mirror, without damage to the ULE substrate. At this time, the specific coating has not been decided, so this report has been written to cover all the possibilities, which are listed here: (a) Bare aluminum (Al); (b) Silver protected with hafnia (Ag/HfO_2); (c) Silver protected with silicon nitride (Ag/Si_3N_4). ULE is comprised of 92.5% silicon dioxide and 7.5% titanium dioxide; a highly chemically-resistant combination. This will be a benefit to the procedures, as both HfO_2 and Si_3N_4 are very durable and tough to remove.

There are several different methods of removing a coating from a mirror surface. These are (a) Liquid Etching, (b) Vapor/Chemical Etching, (c) Laser Etching, and (d) Soluble underlayers. The conventional liquid etching method involves manually using acids and/or bases to chemically dissolve and remove the coating. Vapor etching is an alternative approach used for many years in the semiconductor and optics research fields, where the surface is exposed to reactive vapor etchants while under vacuum. Laser etching is self-descriptive; a laser set at a certain energy is used to create a small plasma field on the surface of the mirror, thereby removing the coating. Soluble underlayers involve a dissolvable layer under the reflective and protective coatings that can be washed away.

A recoating schedule of every two years has been discussed, with a time limitation of 2 days from mirror and cell removal to reinstallation in the telescope. This means that whatever process is decided upon, it must be able to be completed with a limited amount of time. [This time constraint may be physically impossible to meet, since most of the methods will take at least a day (if not more), and the removal and reinstallation of the mirror and cell are also included in this time limit.] Other considerations for the process are: safety, cost, ease of implementation, and interaction with other systems in the enclosure (such as ventilation and power). All of these will be discussed in more detail in a later section.

Review of Liquid Etch Methods

The traditional method that has been used by observatory coating engineers for a long time is a liquid etch, also known as chemical bath etching or chemical removal. It involves putting various chemicals on the mirror surface, manually rubbing with Kimwipes or Texwipes, rinsing with distilled water, and repeating. Stripping a 1m mirror takes most of 4 or 5 hours, and stripping a 3.5m or 4m mirror is a whole-day event. (This is <u>just</u> coating removal, not the actual recoating.) Table 1 shows what chemicals are involved in a liquid etch, the conservatively estimated amounts needed for an 8m mirror, and the procedure involved. The process listed below, obtained from Jon Settlemyre at KPNO and modified for silver by Don Kucera at NOAO, will remove both aluminum and silver; chemical D will remove the chromium adhesor layer for silver.

Table 1. Standard Procedure for Coating Removal

Chemical A:	13.6 kilograms hydrochloric acid, reagent grade (37%). 1.13 kilograms cupric sulfate, reagent grade. Place in appropriate container and add distilled water to make 50 liters. Agitate until dissolved.
Chemical B:	.946 liters potassium hydroxide, reagent grade. Place in appropriate container and add distilled water to make 20 liters. Agitate until dissolved.
Chemical C:	2.72 kilos nitric acid, reagent grade (70%). Place in appropriate container and add distilled water to make 10 liters.
Chemical D:	To 6 liters distilled water, add 1.65 kilograms ceric ammonium nitrate, reagent grade, and 900 milliliters of nitric acid, reagent grade (70%). Agitate until dissolved, then add enough distilled water to make 10 liters.
Chemical E:	Calcium carbonate, reagent grade. Enough for neutralizing several times over.
Chemical F:	Distilled water. (60-70 gallons)
Other :	Assorted solvents such as methanol, propanol, and acetone; gaseous nitrogen.

WARNING: APPROPRIATE CHEMICAL GEAR MUST BE WORN AT ALL TIMES.

1. Rinse mirror with F.
2. Use A, rub with Texwipes.
3. Rinse well with F.
4. Use E, rub with Texwipes.
5. Rinse well with F.
6. Sprinkle E on mirror, use B, rub with Texwipe.
7. Rinse well with F.
8. Repeat steps 6 and 7 three to four times.
9. Rinse mirror with C.
10. Rinse mirror with F for 5-10 minutes (appropriate to area)
11. Dry thoroughly with Texwipes, including sides and bottom.
12. Use filtered gaseous nitrogen to blow off lint, dust, etc. from mirror
13. Inspect surface for soils using appropriate equipment; use solvents as necessary to remove fingerprints, smudges, etc.
14. If anything is left on mirror, go to step 5 and repeat.

For the protected silver coating, other chemicals may be required. Table 2 shows the various chemicals that will react with the possible overcoatings, and some alternate chemicals that will etch silver.

Table 2. Liquid Etch Possibilities[2]

Etching Ag:	(1) Equal amounts of water and concentrated nitric acid (HNO_3). This is a good possibility, as it also etches many oxides, nickel chromium (NiCr), and silicon nitride (Si_3N_4). (2) An aqueous solution of ferric nitrate. This is very effective but has a high reactive rate, and would require a very fast rinsing period.

(3) Water, potassium iodide (KI), and iodine (I_2) in a 4:4:1 solution. This is another fast etch solution.
(4) Ferricyanide and sodium thiosulfate. (No comments made.)

Etching Si_3N_4: (1) Same as (1) above.
(2) Concentrated hydrogen fluoride (HF). A moderate reaction time.
(3) Hydrogen fluoride (HF) and nitric acid (HNO_3) in a 3:10 solution. This method involves using molybdenum (Mo) or chromium (Cr) masks.
(4) Hot (above 350 ^oC) phosphoric acid (H_3PO_4).
(5) Various compound etchants, including HF:HNO_3, HCl:HNO_3, and others.

Etching HfO_2: There are very few etching methods available for hafnia. Possibilities:
(1) Hydrogen fluoride (HF). Very, very slow.
(2) By analogy with zirconia, sulfuric acid (H_2SO_4) and water in a 2:1 solution.

Adhesor Layers: (1) Nichrome can be removed by HNO_3, HCl, and water in a 1:1:3 solution. Also, ferric chloride solutions and an equal mixture of HCl and water at 50 C have been used.
(2) Chromium can be removed the same way.

Review of Vapor Etch Methods

Vapor etching can fall into several categories: glow discharge cleaning, DC and RF sputtering, reactive ion etching (RIE), ion beam etching (IBE), reactive ion beam etching (RIBE), or plasma ashing. A brief summary of each follows.

(a) Glow discharge cleaning is what is currently done in the 4m tank at KPNO. The process cannot remove films, only minor contamination. It is usually used as a last, final-clean step before the actual coating process.
(b) DC sputtering involves striking a plasma with a DC power supply between the substrate and another electrode. An inert gas in the chamber will produce deposition, but by using a reactive species you get a material removal. This method can be tailored for selectivity, but it requires that the substrate be conductive (or other methods are used to overcome charging effects).
(c) RF sputtering is the same general idea as DC sputtering, but a radio frequency transmitter is used to generate the plasma. This allows greater control, and a greater range of materials that are able to be etched. Using an inert gas, the process is referred to as RF diode sputtering; using a reactive gas, it is reactive ion etching. RIE is highly utilized in semiconductor fabrication because there is no substrate charging involved.
(d) Ion beam etching involves using ion guns to direct a stream of ions to the surface, "blasting" the coating off of the substrate. IBE will etch almost anything, but is expensive to implement.
(e) RIBE is a combination of these two processes, and is considered the most technically delicate.
(f) Plasma ashing uses an oxygen plasma to "burn off" the hydrocarbons.

Many semiconductor research groups use one or more of these methods for removal, including Sandia National Laboratories, Intel, AT&T, the Center for High Technology Materials at UNM, Hughes-Danbury, DEC, and many, many more. Because the principal area of interest to date has been semiconductors, most of these processes (except for (a)) have been done only on a small scale. However, researchers at both Sandia Labs and CHTM believe that a scaling-up of these processes is feasible.

Review of Laser Etch Method

The same system designed by STI Optronics to in-situ clean the mirror can also be modified for use to strip the coating from the mirror. This process has also been done at Sandia Systems, Inc., and the Center for High Technology Materials at UNM, as well as other semiconductor research groups.

Following the information put forth by STI[3], the amount of laser energy needed to clean the mirror surface is several times lower than the threshold for damaging the coating. This means that by increasing the laser fluence it is possible to remove the coating with no damage to the substrate. The UV laser beam would create a near instantaneous heating of the mirror coating, which creates a small plasma. This detaches the coating from the substrate and also imparts enough energy to the detached particles to "pop" them off the surface. The easiest way to increase the laser fluence in this process is to reduce the laser beam spot size. Particle and dust removal is an issue with this method; however, using a vacuum with a long nozzle should accomplish this.

Through laboratory tests it has been determined that a single laser shot with energy of 2.2 J/cm^2 (or more shots at a lower fluence) will remove aluminum from a silicon wafer[4]. There is little data available about the possible effects of an intense laser beam on a substrate of ULE; however, extensive studies involving high-intensity excimer lasers and ceramics, and data available for laser cleaning of Al_2O_3, indicate that the laser stripping process will not damage the ULE substrate. This process could be combined with a glow discharge process in the coating chamber for maximum effectiveness; it would also be easy to implement with the in-situ laser cleaning system. If this method is chosen for the Gemini Project, an additional experimental phase must be implemented to study the process as applied to the relevant materials.

Soluble Underlayers

This process has been used quite a lot in semiconductor and small optic research at Sandia National Laboratories. It involves putting down a thin layer of a soluble material under the coating and protective overlayers. When the time comes for coating removal, a simple stream of appropriate liquid is applied to the side of the mirror and dissolves the underlayer, thus removing the coating. There are many options to use that are water-soluble, but this option may be more trouble than not. Water is a presence in any telescope dome, in many different ways; this option would prove to be a weak point in the coating and should be disqualified. However, there are other options that are soluble in other liquids; according to Dr. Robert Blewer, Sandia Labs, the most prevalent is a thin layer of tungsten. Tungsten is soluble in hydrogen peroxide (H_2O_2), a material that is not usually present in a dome environment. Adding another target to the sputtering chamber to put down this layer would be a minor adjustment; and that would be the only change necessary. When it is time to recoat, the mirror would be set on the stripping support system already under design, and simply washed off with H_2O_2.

Discussion of Each Method

<u>Liquid Etch.</u>

Silver and aluminum will not pose a specific problem; neither will the adhesor layers. The proposed overcoatings may be a bit more difficult. The substrate itself is highly resistant to nitric and hydrochloric acids, so removing the Si_3N_4 should not be difficult; however, it is extremely reactive with hydrofluoric acid, so that will not be able to be used to remove the HfO_2. The concurrent Protected Silver

Coatings Program (PSCP) will investigate all of these possibilities. Based on initial results from the PSCP, weaker solutions may be used in place of the stronger ones, as the coating layers are actually very thin and can be attacked by a weaker acid.

This method is known to work, and has been used in the astronomical community for decades. However, the amounts and types of chemicals required is a serious safety hazard. It would be desirable, for this method, to have a full ventilation system of 3.5 m^3/s (7,500 c.f.m.),a maintained positive pressure differential to aid room cleanliness of at least 140 Pa, or 0.02 psig[5], and an interior wall wash-down. Full chemical suits for all personnel would be required. It is a lengthy process; manually stripping, rinsing, and drying of an 8m mirror can take over 12 hours. It will require some kind of mechanical interface to cover the inner ring of the mirror that can't be reached by people, such as the machine design currently being investigated by Paul Giordano at ESO. Scaling this process may be a major problem.

<u>Vapor/Chemical Etch.</u>

For the Project's purposes the RIE process might be best, as it would be easiest to interface with the existing coating setup and causes no additional charge buildup to the substrate. They also all function at a low vacuum, as compared to the ultra-high vacuum the coating process will be run at; therefore, a two-phase coating removal/recoat program could easily be implemented. All of these processes result in particulation within the vacuum tank (particulate sizes ranging from 1-50μm), but this material can become trapped in the gas flow and is discharged from the chamber with further pump-down. If a vapor etch process is chosen for Gemini, the particulation problem cannot be ignored, as particle contamination caused by plasma processes generally exceeds that of other process steps, and greatly exceeds the contribution from handling and clean-room exposure. However, with careful attention to process details, this particulation can be removed from the tank. Researchers at IBM[5] have found that a gentle rf power ramp-down prior to plasma shut-off caused the particles to float harmlessly to the pump ports, while an abrupt plasma switch-off caused substrate contamination.

One particular benefit of the vapor etch program is that a milder family of chemicals can be used to etch the coating. Since the coating thicknesses are so thin, in a reactive environment a less corrosive chemical can be used, for all options. This avoids any possibility of using HF, one of the most dangerous chemicals, and the only one that does substantial damage to the substrate. It also means that a lower power of HCl or HNO_3 could be used.

This method has been used for years in industry; scaling should not be a problem. It means there will be fewer chemicals in storage, and it will be safer for personnel (it is a contained process and requires minimal exposure to hazardous chemicals). It is fast; the entire procedure theoretically can be completed well within the time limits set by the Science Requirements. Modifications to the tank would be minimal; the same vaccum ports and pumps can be used to remove the coating as are used for the coating process itself.

<u>Laser Etch.</u>

Modification to existing laser system would be minimal; using the laser to strip the coating would simply require a program change. There is no direct data on possible harm to substrate, but by extrapolation from tests done on other, similar materials it is unlikely. The process does leave 'dust' on the mirror surface, but it is possible to remove this dust using vacuum ports.

Soluble Underlayer.

This process works at a small scale, and has been used in the semiconductor arena for years. There is no data as to whether increasing the scale might be a problem, but researchers at Sandia National Labs see no reason why it would be. The chemicals used are almost completely neutral, so full chemical suits would not be required and personnel would be safe. The process is rapid at a small scale.

Special Note.

Three of the mentioned methods require an additional step before the mirror is placed into the coating chamber. Using a laser etch, the mirror would have to be rinsed to remove the dust; for both the liquid etch and the soluble underlayer methods, the last step would be a distilled water rinse. This requires that the mirror be completely dried before being placed into the chamber. This introduces some problems. If liquid etching is chosen and a machine is designed to aid in removal, that same machine could be used to aid in drying the upper surface. However, for the laser etch and the soluble underlayer, a method would have to be determined to dry the unreachable ring in the middle of the surface. All three methods would also require the lower surface of the mirror to be dried, and that is a major problem. OSHA regulations prohibit suspending the mirror and working under it; the mirror would have to be dried while resting on the support stands. These stands may only be one or two feet off the floor; for personnel to crawl on the floor under the mirror, between the support stands, to dry the undersurface is unsafe. However, a compressed air system for drying may be a solution.

Table 3. Base Comparison of Each Method

Liquid Etch	**Vapor Etch**	**Laser Etch**	**Soluble Underlayer**
high volume of chemicals	low volume of chemicals	no chemicals	low volume of chemicals
requires additional means to implement - i.e. ESO's stripping machine	can be easily implemented into existing equipment	can be easily implemented into existing equipment	can be easily implemented into existing equipment
requires drying	no drying	requires drying	requires drying
special ventilation needs	no special ventilation needs	no special ventilation needs	no special ventilation needs
full chemical suits required	no safety gear requirements	safety goggles required	no safety gear requirements
high initial cost, middle maintenance cost	high initial cost, low maintenance cost	middle initial cost, low maintenance cost	low initial cost, low maintenance cost

Summary and Conclusions

Removing the coating from the mirror is not a trivial process; clean, safe removal is crucial to a smooth, correct, fresh coating. Based on initial investigation into the possible processes for removing a coating from the Gemini 8m primary mirror, the best option would be an RIE process. Using a liquid etch process is potentially dangerous when scaled up to an 8m substrate, and is a lengthy process that would not meet the science requirements. If a mechanical system such as the one that ESO is investigating is adopted, then the time factor may be reduced, but the chemicals involved remain the same and the mirror would still require a thorough manual drying. The laser etch method may be ideal, but since there is no empirical data, it would require a thorough laboratory research to determine any effects to the substrate, and the ideal energies for removal. Utilizing a soluble layer under the coatings may be a possibility, but again there is no specific data and a complete research program would have to be instigated. It is, however, the second best option in terms of safety.

The reactive ion etch process is the only process, based on available data, that can be completed within the necessary time frame. It is also the safest process, as it is completely contained within the coating chamber, and requires only a small amount of chemicals (that are contained in tanks) to complete the process. Modifications are minimal; only filtration units for the pumps would be needed since the same inlets and outlets can be used and the tank and fittings are already designed of resistant material (stainless steel and Viton fittings).

The currently ongoing Protected Silver Coatings Program will determine what chemicals will remove the coatings from the substrates at a small scale. Whatever process is chosen will require further laboratory investigation to determine the proper amounts for an 8m mirror, and (if RIE is chosen) the correct reactive chemistries.

References and Acknowledgments

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