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CHEMICAL REMOVAL OF OPTICAL COATINGS.(U)
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CHEMICAL REMOVAL OF OPTICAL COATINGS

E. W. Wasson

August 1979

Final Report

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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

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fluoride and zinc selenide were removed from substrates of molybdenum, titanium-zirconium-molybdenum alloy, germanium and silicon.

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SUMMARY

The removal of thin-film optical coatings is required in the fabrication of optical components and when refurbishing used components. Chemical removal is quicker and less costly than removal by polishing. With the proper choice of chemical reagents, many coatings can be removed without damage to an optical quality substrate. However, reagents and conditions must be carefully chosen, the production of toxic materials must be minimized, and the least corrosive reagents must be utilized. Some of the most common infrared thin-film materials and optical substrates are considered in this report. This research is continuing and will cover a broader range of substrates and coatings used at infrared wavelengths. Methods of removing coatings used at near infrared, visible and ultraviolet wavelengths will also be attempted.

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INTRODUCTION

Valuable optical components coated with metallic or dielectric materials often require coating removal during fabrication or refurbishment. This process has traditionally been done by optically polishing the component until the substrate is revealed. The polishing process requires expensive equipment, highly skilled personnel, and large amounts of time. The same result can be obtained by chemical removal of the coatings in many cases.

In a research program that was specific to common, infrared laser components, both transmissive and reflective optical substrates were considered. Widely used infrared coating designs were applied to germanium, silicon and zinc selenide windows, also to molybdenum and titanium-zirconium-molybdenum (TZM) mirror substrates. The coating design consisted of one or more metals and dielectrics such as chromium, silver, gold, thorium fluoride, zinc sulfide and zinc selenide. Test pieces were fabricated for testing purposes. Actual laser components were also used to test the effectiveness of the procedure. Substantial differences were noted in freshly coated samples and damaged laser components. The test procedures work well with freshly coated samples, but coatings are usually much more slowly and less completely removed on a damaged component.

Not all layers of a coating necessarily require removal when refurbishing an optical component. Using chemical selectivity, certain layers can be removed leaving the remaining layers intact. Thus, some coatings do not require reapplication in such a procedure.

TEST EQUIPMENT, COMPONENTS AND CHEMICAL REAGENTS

The effectiveness of coating removal was evaluated in three ways: transmission/reflectivity measurement, coating thickness measurement, and visual inspection. A Fourier transform spectrometer with a wavelength range of 2.5 to 22.2 μm was used to measure transmission or reflectivity. A Taly-Step* thickness measuring device utilizing a precision stylus was used for thickness measurement of fabricated coatings; this device measured thickness to an accuracy of $\pm 20 \text{ \AA}$. While for some test pieces, visual inspection was used to determine coating removal, this procedure is not effective for many dielectric materials. All test pieces were fabricated in-house using vacuum deposition with an electron-beam heating source.

Optical components used for substrates were commercial microscope slides, germanium and silicon wafers, zinc selenide windows and molybdenum or TZM mirrors fabricated in the Air Force Weapons Laboratory.

Chemical reagents used in the research program were of specified purity standards to the extent that no technical or practical grade reagents were used. Deionized and distilled water was used for washing.

*Taly-Step is a registered trademark of Rank Industries.

CHEMISTRY OF SUBSTRATES, COATING MATERIALS AND REAGENTS

Chemical reagents used for coating removal must remove coatings while not affecting the substrate. Moreover, the use of corrosive or toxic materials must be minimized or avoided. The production and disposal of the products of coating removal must be considered since toxic materials may be produced and corrosive materials will not generally be totally consumed during coating removal. This requirement determines the necessity for: a water-scrubbed hood system; acid drains; solid-waste disposal procedures; and special training for operating personnel.

The mirror substrates most commonly used are molybdenum and TZM. Both are similar in their chemical reactivities (ref. 1). They are not attacked by hydrochloric, hydrofluoric or sulfuric acids. Nitric acid attacks the surface before rendering it passive. Mixtures of hydrochloric and nitric acids, or hydrofluoric and nitric acids, slowly dissolve molybdenum. Alkaline solutions should be avoided since attack occurs if oxidizing agents are present. Fluorine reacts with molybdenum at room temperature. Both chlorine and bromine attack at temperatures above 325°C, but iodine does not react (ref. 2).

Germanium does not react with hydrochloric acid but is superficially attacked by hot, concentrated sulfuric acid and by concentrated nitric acid. Strong alkaline solutions attack weakly. Sodium hypochlorite reacts with germanium to form germanium dioxide. Germanium absorbs water and alcohol. When water is absorbed and the germanium is heated, an oxide film forms on the surface. The element burns in chlorine and bromine, and reacts slowly with iodine to form orange germanium iodide (ref. 3).

Silicon in pure crystals is inert to all acids, including hydrofluoric. Most silicon contains impurities which catalyze reaction, particularly in basic solutions, and with most acids. Fluorine, bromine, chlorine and iodine all attack silicon. There are distinct differences in the reactivity of silicon depending on its purity. The pure material is completely inert to water, acids and oxygen, while impure silicon is reactive. Molten silicon is extremely reactive and can only be contained in crucibles of zirconium oxide or some transition metal borides. Silicon reacts with many solids to form silicides or eutectics. Both mercury and bismuth are completely immiscible with silicon, even in the liquid state. Germanium forms a continuous range of solid solutions with silicon.

Zinc selenide is insoluble in water, but reacts with dilute acids and iodine. The reaction with dilute acids results in the production of hydrogen selenide. This product has a maximum allowable exposure (8-hour weighted average) of 0.05 part per million (p/m). The reaction with zinc selenide and iodine results in metallic selenium, which is relatively nontoxic (ref. 4) and easily disposable as a solid. Zinc sulfide undergoes an analogous reaction, resulting in the production of sulfur.

Thorium fluoride is slightly soluble in water, and insoluble in acids, even hydrofluoric.

Chromium reacts with sulfuric, hydrochloric and hydrofluoric acids. It does not react with phosphoric acid. Chromium is rendered passive by nitric acid or aqua regia, or other oxidizing media. However, there is an initial attack. Passive chromium can be made active by a reduction process such as treatment with hydrochloric acid in contact with zinc or some other active metal.

Gold reacts with aqua regia or potassium cyanide, and amalgamates with mercury. When gold reacts with potassium cyanide, the solution should always be kept alkaline to preclude any production of hydrogen cyanide. The maximum allowable exposure (8-hour weighted average) for hydrogen cyanide is 10 p/m. The addition of hydrogen peroxide in trace quantities, or mixing of the solution with air, accelerates the rate of reaction. Gold can be amalgamated with mercury to provide 0.13 percent by weight of gold in mercury at 20°C.

Silver reacts with dilute nitric acid and concentrated sulfuric acid. Silver also amalgamates with mercury to provide 0.03 percent by weight of silver in mercury (ref. 5).

Aluminum reacts with alkaline solutions which break down the aluminum oxide layer and react with the base metal. Aluminum reacts vigorously with iodine or bromine. This reaction is easily moderated with solvents which do not contain hydroxyl groups (ref. 6).

COATING REMOVAL ON TEST PIECES

1. A microscope slide was coated with 1000 Å of zinc selenide. Treatment with alcoholic iodine gave complete removal in 30 minutes. Thickness measurements were done before and after coating removal with a Taly-Step thickness measuring instrument to an accuracy of ± 20 Å.
2. A molybdenum mirror of 1.5-inch nominal diameter was immersed in an alcoholic iodine solution for 24 hours. Measurements of surface roughness and reflectivity showed no discernible change.
3. Chromium and gold, respectively, were coated on a 1.5-inch diameter molybdenum substrate. The gold was removed by amalgamation with mercury by swabbing a drop of mercury across the surface. Amalgamation was immediate and complete by visual inspection. The chromium was removed immediately with concentrated hydrochloric acid. The surface roughness was lower and the reflectivity was higher after coating removal than before.
4. A thorium fluoride coating of 6800 Å on a quartz substrate was removed within 2 minutes by running water at 55°C.
5. A molybdenum substrate was coated with chromium, gold, thorium fluoride and zinc selenide, respectively. Treatment with alcoholic iodine, hot water, mercury and hydrochloric acid, respectively, gave complete removal as determined by a total thickness measurement.
6. Germanium substrates coated with zinc selenide were treated with alcoholic iodine resulting in extreme corrosion of the germanium surface. Treatment of the same combination with dilute hydrochloric acid removed the zinc selenide and did not attack the germanium.
7. Quartz substrates coated with silver were washed with dilute nitric acid, giving immediate removal of the silver as determined by visual inspection.
8. Pyrex substrates coated with aluminum were treated with potassium hydroxide, resulting in coating removal in 1 hour provided the surface was swabbed occasionally.
9. TZM alloy mirrors were treated with alcoholic iodine and hydrochloric acid, respectively, and showed the same corrosion resistance as molybdenum.

Table 1 lists the materials and reagents used for the coating removal tests and indicates the materials that showed reaction.

TABLE 1. MATERIALS AND REAGENTS TESTED

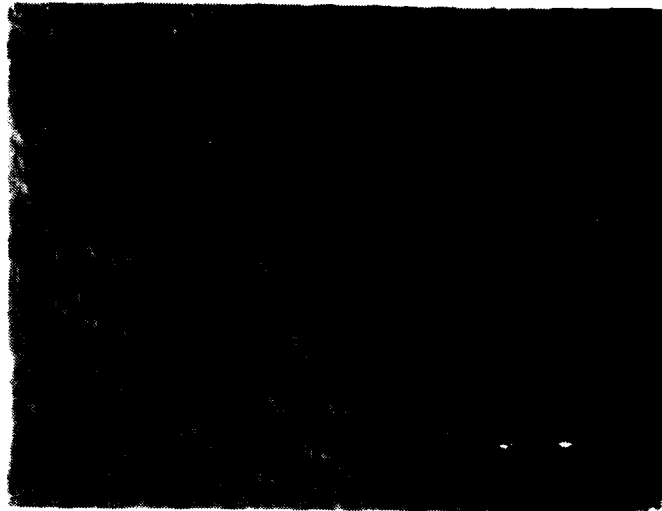
REAGENT	MATERIAL									
	Al	M _o	Cr	Ag	Au	Ge	Si	T _h F ₄	Z _n S	Z _n Se
KOH	X						X			
HCl	X		X	X			X		X	X
HNO ₃	X	X		X		X	X			
H ₂ SO ₄	X		X	X	X	X	X		X	X
AQUA REGIA	X	X		X	X	X	X		X	X
I ₂	X				X	X	X		X	X
Hg				X	X					
H ₂ O						X	X	X		
HF	X		X				X		X	X
KCN				X	X					
H ₂ O ₂		X				X				

X Indicates Reaction

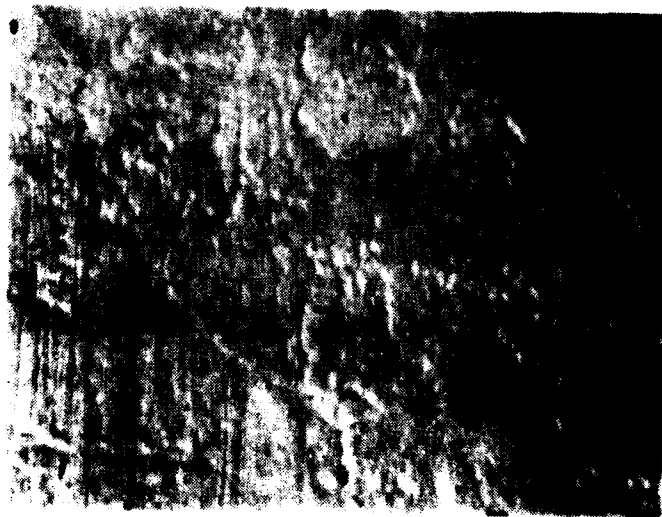
COATING REMOVAL ON OPERATIONAL OPTICAL COMPONENTS

Two water-cooled molybdenum mirrors with a coating design of chromium binder layer, gold reflectance layer, and dielectric reflectance enhancement coating of thorium fluoride-zinc selenide_n (where $n = 4-20$) were treated with iodine until a consistent surface quality was obtained. This required three treatments. The mirrors were then immersed in running water for 30 minutes. The entire procedure was repeated until the gold coating was exposed. Hydrochloric acid removed the chromium in approximately 15 minutes. One of the mirrors had a pronounced burn spot of approximately 2.5 cm diameter, and did not leave an evenly reflective surface.

Nomarski photographs (figures 1 and 2) show the mirror surface before and after removal of the coatings.

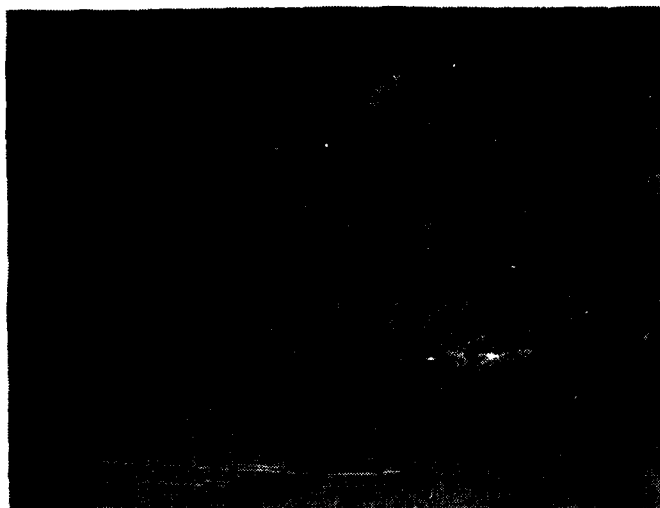


a. Before treatment

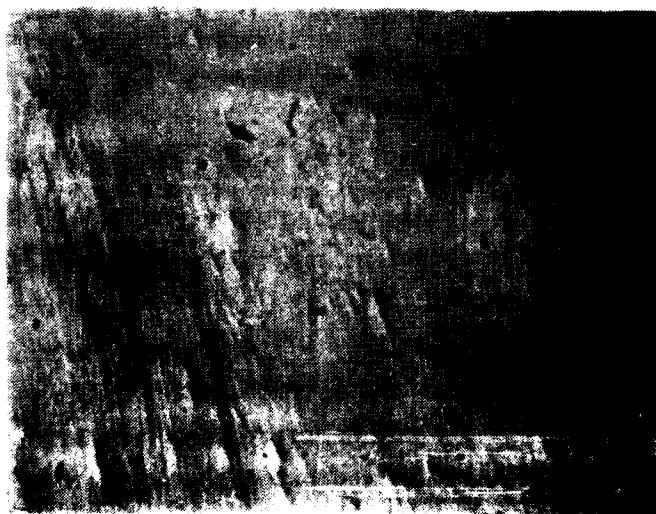


b. After treatment with hydrochloric acid

Figure 1. Molybdenum mirror with coating of 2000 Å chromium and 1000 Å gold.



a. Before treatment



b. After treatment with iodine,
water and hydrochloric acid.

Figure 2. Molybdenum water-cooled mirror with coating of chromium-silver (thorium fluoride-zinc selenide)_n

CONCLUSIONS AND RECOMMENDATIONS

1. On the basis of the designs tested, test pieces and operational optical components which do not have coating damage can successfully be stripped of their coatings. However, damaged coatings leave an imprint on mirror surfaces, and the coatings are difficult to remove.
2. Procedures were verified which are useful for reclaiming undamaged components. This situation occurs when a coating process does not give the required optical specification and must be recoated, or when an undamaged component substrate is reclaimed for another use. Selective removal allows removal of certain layers while leaving the remaining layers intact.
3. A reasonably complete facility has been established for chemical coating removal. This facility is useful for continued research in coating removal and for fast response in coating removal of optical components which may need fabrication in a very short time.
4. More evaluation is required in two areas. First, the removal of coatings on damaged components. A complete evaluation of different damaged areas could reveal appropriate methods of chemical removal of coatings. Second, when only the dielectric stack is removed, the effect of recoating on the performance of an operational components is unresolved.
5. Other coating designs are uninvestigated, particularly those in the near-infrared and visible wavelengths. These coatings are very difficult to remove since they are usually composed of very stable metallic oxides.
6. One other challenging coating design is a zinc selenide substrate with alternate layers of thorium fluoride and zinc selenide. In theory, it is possible to remove the dielectrics with alternate treatments of iodine and water. If the coating were damaged, this procedure would result in chemical action on the substrate since the substrate would probably be exposed at some points. If the substrate were not damaged, the procedure should work since the thorium fluoride is adjacent to the substrate, and therefore the last treatment would be with water.

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