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UV-Shifted Durable Silver Coating[1] for Astronomical Mirrors

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UV-Shifted Durable Silver Coating[1] for Astronomical Mirrors

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ABSTRACT

Silver has the highest reflectance of all of the metals, but it tarnishes in the presence of sulfides, chlorides, and oxides in the atmosphere. Also, the silver reflectance is very low at wavelengths below 400 nm making aluminum more desirable mirror coating for the UV region. We have found a way to prevent silver tarnishing by sandwiching the silver layer between two thin layers of $NiCrN_x$, and to extend the metal's high reflectance down to 200 nm by depositing the (thin) Ag layer on top of Al. Thus, the uv is transmitted through the thin Ag layer below 400 nm wavelength, and is reflected from the Al layer underneath. This UV-shifted durable coating[1] provides a valuable alternative to the aluminum coating for telescope mirror coatings where high throughput and durability are important considerations. The throughput for a telescope with, say, six reflections from silver coatings is $(0.97)^6 = 83\%$ compared to $(0.92)^6 = 60\%$ for aluminum coatings, or 28% less. The use of silver coatings allows more photons to be collected by primary mirror. Aluminum also has a reflectance dip at 850 nm caused by inter-band transitions which is eliminated by placing the thin Ag layer on top. This paper describes a non-tarnishing silver coating having high reflectance down into the UV region. The average specular reflectance is 70% - 97% in the near-UV, 95% - 99% in the visible region, and ≥ 99% in the infrared region covering the total wavelength range 200 nm to 10,000 nm. Figure 1 compares the reflectance of our UVHR-LLNL silver coating to bare silver and aluminum over-coated with magnesium fluoride over the wavelength range 300 nm to 2000 nm.

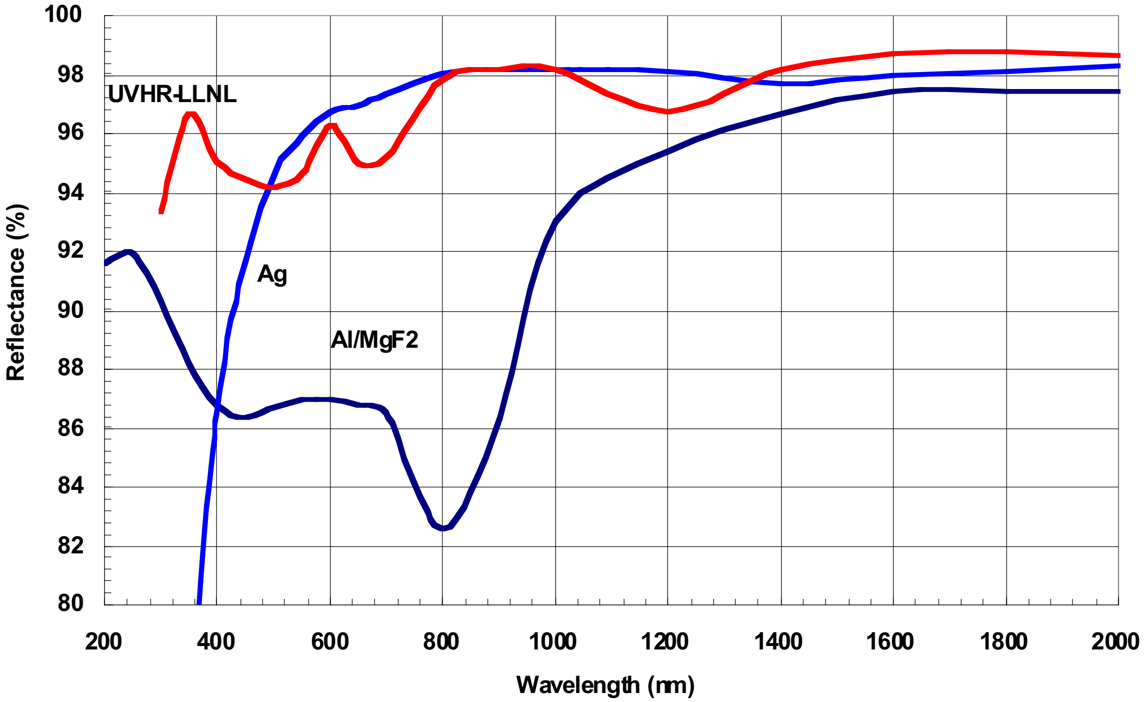


Figure 1-Reflectance of Al/MgF2, Ag, and UVHR-LLNL vs Wavelength

Key words: silver coating, uv coating, thin film, Al, Ag, astronomical mirror coating, uv-shifted silver, non-tarnishing.

1. INTRODUCTION

Evaporated silver on mirror substrates has several advantages compared to other metals. It has the highest reflectivity from 400 nm through the infrared and the lowest polarization splitting compared to any other metal. Figure 2 compares the reflectance for silver, aluminum and gold. The disadvantage of bare silver is that it tarnishes under ordinary atmospheric conditions and does not have a high reflectance below 400 nm. There is a minimum reflectance at 320 nm due to a surface plasmon resonance. Aluminum, on the other hand, has a dip in reflectance at 850 nm due to inter-band transitions[3], but reflects well down to 280 nm, the cutoff for atmospheric transmission. If a thin layer of silver is deposited on aluminum, the advantages of silver and aluminum are combined: silver reflects for $\lambda > 400$ nm and masks the dip at 850 nm, and aluminum reflects for $\lambda < 400$ nm where silver is semi-transparent[1].

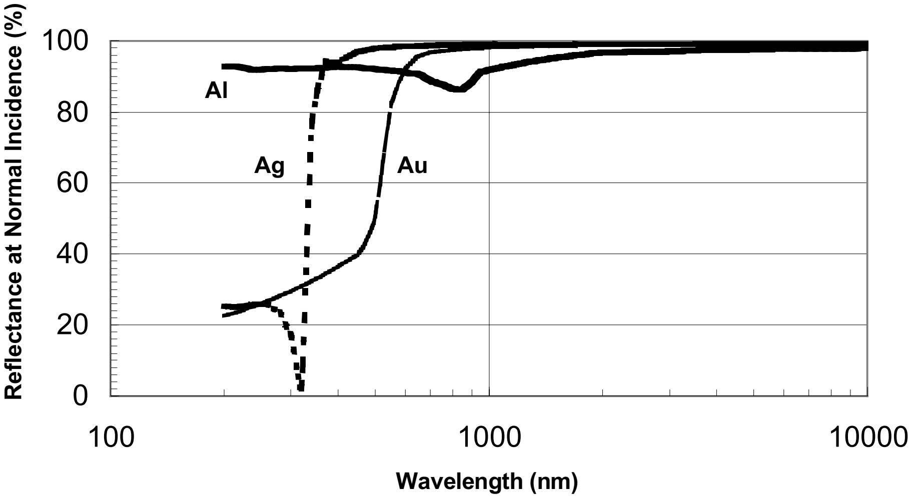


Fig. 2 Reflectance of evaporated metals in the visible and infrared.

Silver is a noble metal which is completely stable in aqueous solutions of any pH as long as oxidizing agents or complexing substances are not present. In the presence of such substances, the high specular reflectivity of silver is degraded by sulfidation, chloridation and oxidation with corrosive chemicals[4-14] in the atmosphere such as H_2S, O, $O^{=}$, H_2O_2, SO_2, CL^-, etc. The corrosion products of silver are Ag_2S, AgCl, Ag_2O, Ag_2SO_4 and Ag_2CO_3 in increasing order of solubility. Since these products form in the thin water layer which is typically present on silver, the most likely precipitate is Ag_2S. Depending on its thickness, an absorbing Ag_2S film can reduce the Ag reflectance to zero. Similarly, the other corrosion films can reduce the reflectance of Ag. For example, AgCl can photolytically decompose in the presence of light leaving metallic Ag which is the basis for some photographic films. The reflectance of an Ag_2S film grown on Ag versus film thickness is shown in Fig. 3 for three different wavelengths: 450, 500 and 650 nm.

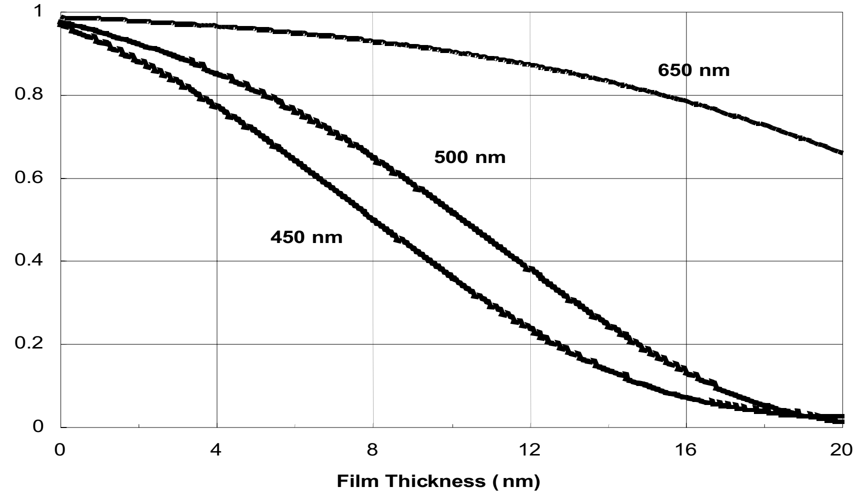


Fig. 3 Reflectance of Ag2S film on Ag versus film thickness

We conducted an Ag corrosion experiment which showed that the growing film reduces the reflectance more strongly at the shorter wavelengths in complete agreement with theory (Fig. 2). For physical film thicknesses approaching 20 nm, the reflectance of silver can be reduced to zero. Severely tarnished silver will appear black under these conditions.

2. IMPORTANCE OF COATING TO ASTRONOMY

The UV-shifted silver coating[1] is extremely interesting to the astronomical community because it maximizes the efficiency over a wide band of wavelengths of interest for astronomical science. More pragmatically, it is the wavelength range covered by silicon charge coupled devices (CCD) detectors, a commonly used detector for many astronomical applications. Since CCDs typically span 300 nm to 1000 nm, it is important that all optics be reflective in order to maximize efficiency while reducing chromatic effects. Thus, the efficiency of coatings is generally important for the success of the instruments.

With time, CCD technology has now advanced so that the UV end can be extended to 200 nm through a combination of backside illumination, passivation, and HfO anti-reflection coatings. This has, once again, pushed the limits of mirror coatings in order to support the full wavelength range of the detector. The “best” material for the 200 nm to 400 nm wavelength range is still MgF_2 overcoated Al. Unfortunately, this material combination is not too good in the visible and near-IR. Thus, the tradeoff is quite severe between the blue and red ends of CCD sensitivity. In the case of Hubble, Al/MgF_2 is used for optimal blue and Ag is used for optimal red.

For astronomy, the blue end is important for studying the constituents of nearby galaxies and the environment of stars. The red end is equally important, and opens up the distant universe because its light is redshifted. In order to understand what distant galaxies are emitting in their rest frame, we must understand how galaxies that are close to us look in the near-UV. A “panchromatic” view of the sky is being sought in order to provide the key to how structures formed and evolved in the universe.

These coating needs have made the coating problem even more severe for the Wide-Field Camera 3 (WFC3), a fourth generation instrument for the Hubble Space Telescope. Both a UV-sensitizes CCD channel as well as a HgCdTe IR focal plane array have been incorporated to cover the wavelength range 200 nm to 1800 nm. Having an optimal coating over this entire wavelength range will simplify the instrument (by allowing common optics) as well as improving its sensitivity (silver is much better than Al/MgF_2 even in the visible).

The first tests on earlier LLNL coatings indicate that they have great promise. Already, we have optimal performance down to 300 nm, with acceptable performance down to 250 nm. By co-sputtering hafnium and tantalum instead of just tantalum, we are achieving low absorption high index oxide layers which enable us to boost the reflectance at 200 nm.

3. HIGH INDEX OXIDE ALLOY FOR UV APPLICATIONS

Hafnia is the high index material of choice for ultraviolet optical coatings. Alloying hafnia with a higher index material is expected to produce a material of intermediate index. The refractive index is primarily determined by the relative content of the two oxides whether or not the two components of the alloy are miscible or immiscible. In the former case, a homogeneous material will result and, ideally, in the latter case, nanocomposites with a precipitate of one phase in the host of the other can be produced. However, the limit of transparency will be different in the two situations. The higher index material will have a smaller band gap than HfO_2 – for miscible alloys, the position of the absorption edge will move between the extremes of the pure oxide components. In the case of immiscible materials, the absorption edge will be governed by the high index component present in substantially pure form.

We investigated the hafnia/tantala alloy as a possible high index oxide used in conjunction with SiO_2 to enhance the uv reflectance of aluminum/silver for $\lambda < 400$ nm. Alloys were produced by DC reactive sputtering in a 48” X 48” X 60” box coater fitted with two 150 mm pulsed DC magnetron sputter sources. The two sources are mounted in the box coater facing upward and with an angular separation of 40°. The substrates were held in a horizontal rotating fixture (8” above the sources), which passes through the plasma. Preliminary deposition runs were done to establish the appropriate conditions under which the two metal targets could be run to give fully oxidized films at useful deposition rates at a given oxygen flow rate.

The absorption edge of pure Ta2O5 can be shifted to shorter wavelengths by alloying tantala and hafnia. For ground-based telescope applications in the 280-300 nm region, the band gap of the alloy is engineered to position the absorption edge at the atmospheric cutoff. At this point the refractive index of the alloy is substantially higher than that of pure HfO_2 (2.51 vs. 2.12 at 280 nm) offering useful increases in coating performance. J.A. Simpson[3] found that other systems, TiO_2-HfO_2 and Nb_2O_3-HfO_2 do not offer more than Ta_2O_5-HfO_2. His n and k data are tabulated in Table 1 for the tantala-hafnia alloys for the wavelengths 260, 280 and 300 nm:

Table 1

Hf fraction	n260	k260	n280	k280	n300	k300
0.0	2.85	0.2	2.63	0.05	2.47	0.003
0.084	2.8	0.23	2.6	0.025	2.39	0.0025
0.137	2.79	0.19	2.53	0.02	2.38	0.0035
0.21	2.7	0.14	2.51	0.023	2.33	0.001
0.285	2.54	0.09	2.36	0.01	2.23	0.0045
0.331	2.44	0.07	2.26	0.08	2.16	0.0
0.422	2.36	0.05	2.22	0.001	2.14	0.0
1.0	2.16	0.007	2.12	0.006	2.08	0.005

We extrapolated this table down to 200 nm wavelength in order to n and k values to design the enhancement stack (Ta_2O_5-HfO_2/ SiO_2) that goes on top of the silver layer. This coating design was optimized to give the maximum possible reflectance between 200 nm and 300 nm while maintaining the high reflectance from 300 nm to 10 microns.

Fused silica substrates were coated with various compositions of hafnia and tantala. Reflectance and transmittance scans were done on a Cary 5 and used to determine n and k using Film Wizard software. The n and k values vs. wavelength are plotted in figures 4 and 5. Unfortunately, we were not able achieve extinction coefficients low enough below 250 nm to make the alloy useful, and ultimately, we had to resort to pure hafnia in order to achieve the necessary transparency down to 200 nm.

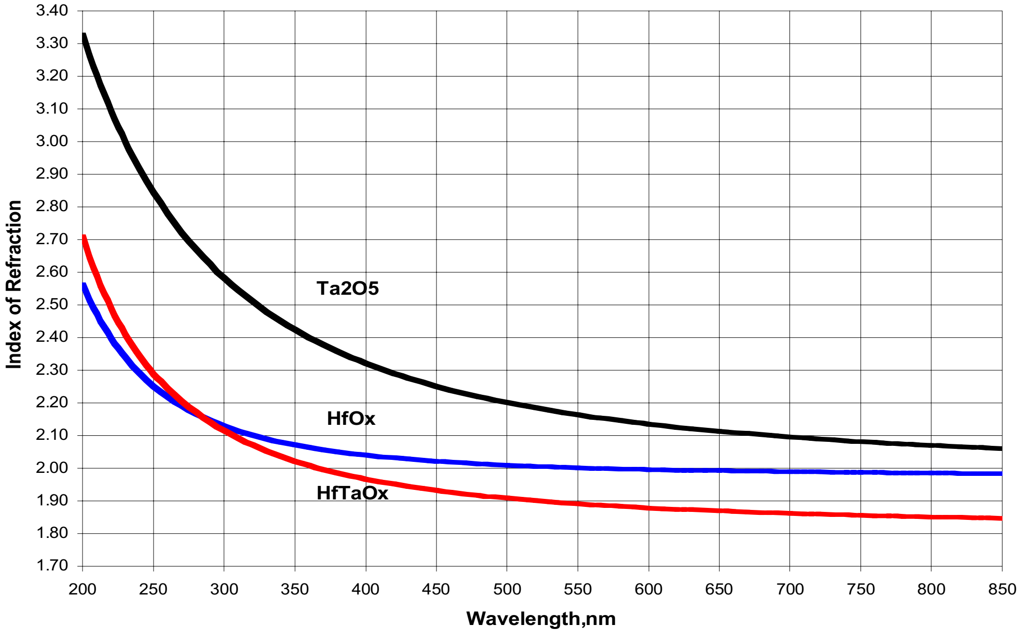


Figure 4 Comparison of the index of refraction for Ta_2O_5, HtO_x and $HfTaO_x$ vs wavelength

Figure 4 shows that the high index alloy $HfTaO_x$ has only a slightly higher index (n) between 200 nm and 300 nm. The alloy has the composition: HfTaOx = 93% HfOx and 7% TaOx . Figure 4 shows that the high index alloy $HfTaO_x$ has a higher extinction coefficient (k) than HfO_x. Therefore, the high index alloy was rejected and HfO_2 was used instead.

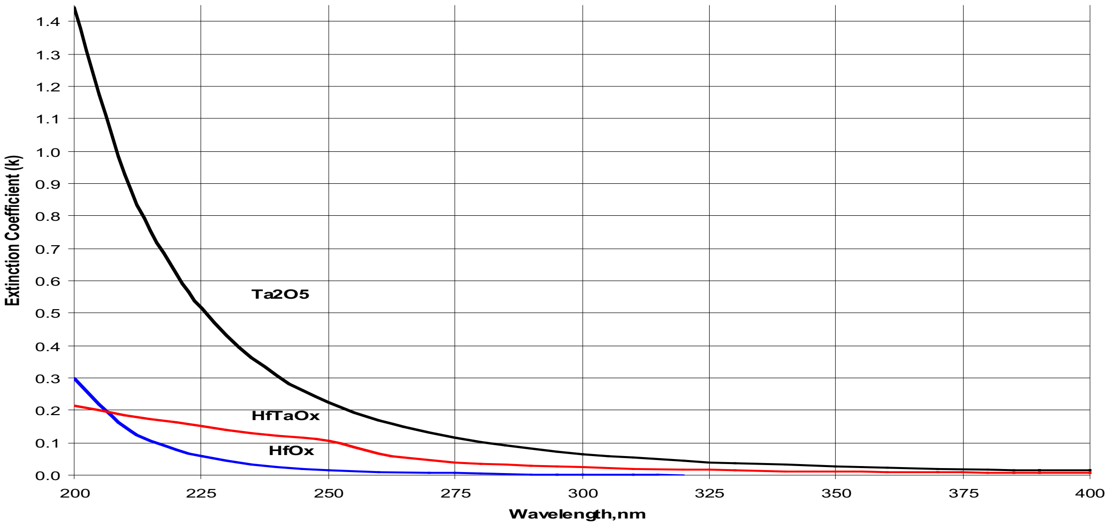


Figure 5 Comparison of extinction coefficient for Ta_2O_5, HfO_x and $HfTaO_x$ vs wavelength.

4. Passivation and Durability Layers ($Ni_xCr_yN_z$ / Si_xN_y)

Many materials besides $Ni_xCr_yN_z$ were tried during the course of experiments. Tests show that no combination of metals tried as passivation / barrier layers provide mechanical and chemical durability equal to that of a $Ni_xCr_yN_z$ / Ag / $Ni_xCr_yN_z$ tri-layer followed by a Si_xN_y layer that was equal to or greater than 30 angstroms in thickness. Experiments proved that a layer of NiCr on each side of a Ag layer had to be 16 angstroms or greater in thickness to provide the same mechanical and chemical durability as a layer of $Ni_xCr_yN_z$ 5 angstroms in thickness.Using the nitrided layer at a thickness of 5 angstroms decreased the amount of absorption in the overall design giving an increase in reflection. This is revealed in Figure 6 below where showing the transmission of 16 angstroms of NiCr vs 5 angstroms of $Ni_xCr_yN_z$ deposited on fused silica substrate.

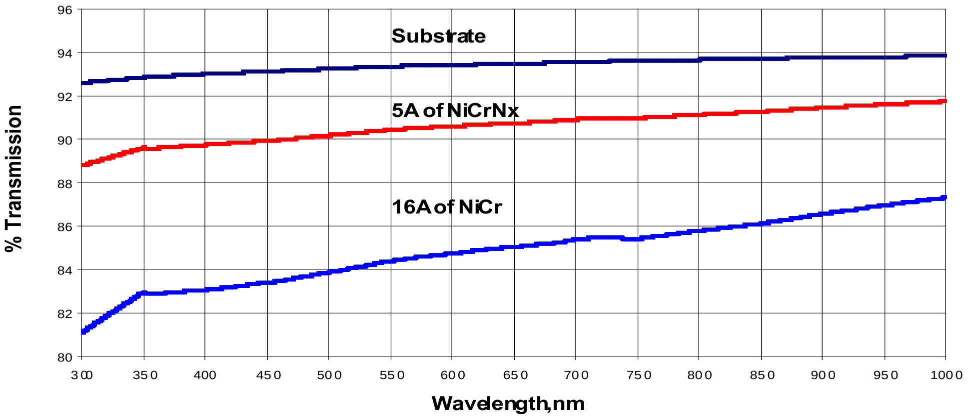


Figure 6 Transmission of NiCrNx compared to NiCr on a fused silica substrate

It is believed that this combination of specific materials works because of the following reasons:

1.) Nickel-chrome (80/20 wt.%) when sputtered in a nitrogen plasma becomes an admixture of nickel and chrome nitride. Nickel does not easily bond with nitrogen, but chromium does. This admixture forms a metal-to-metal bond between the Ag and Ni, while the Cr_xN_y forms a chemical or ionic bond to the following Si_xN_y layer. A phenomenon noticed during the deposition of the $Ni_xCr_yN_z$ and Ag layers is that the sheet resistance of the Ag increases by approximately 20% and the optical absorption increases by 1-2% more than predicted by thin film modeling programs. The new phase mix of the tri-layer causes this absorption increase. Rutherford Backscatter Spectroscopy (RBS) was used to analyze the stoichiometry of a NixCryNz film. The measured stochiometry of the film is $Ni_{0.5}$ $Cr_{0.14}$ $N_{0.36}$ which has approximately the same Ni/Cr ratio as the target.

2.) No combination of barrier layers protecting the Ag even $Ni_xCr_yN_z$ passed the environmental tests, unless a Si_xN_y layer followed the tri-layer with a minimum thickness of 30 angstroms. The only other known non-absorbing transparent nitride, Al_xN_y , was not used since it is water soluble, unless deposited at high substrate temperature.

3.) When oxides were deposited adjacent to the tri-layer without the Si_xN_y layer, the films failed the high humidity and salt- fog tests. It is believed that a plasma containing atomic oxygen disrupts the Ag layer, even when the $Ni_xCr_yN_z$ layer is present. This degradation is especially noticeable during the salt-fog test where deterioration can be caused by stress corrosion cracking.

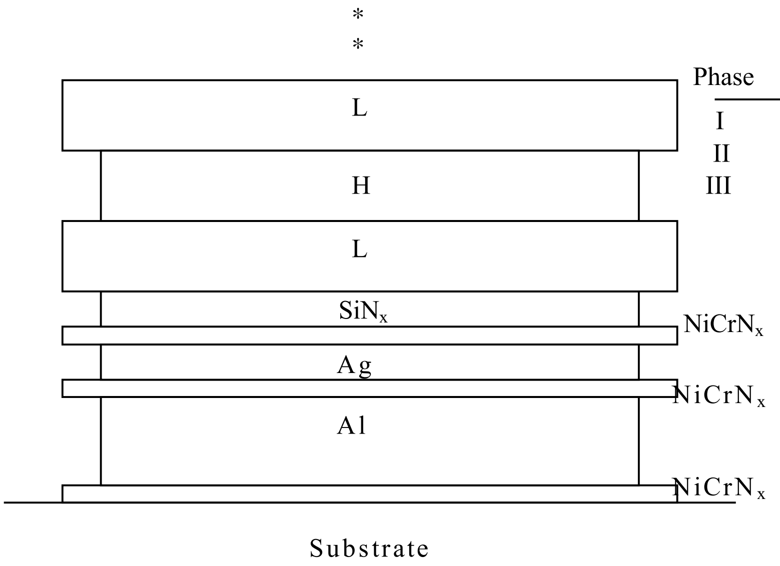
5. THIN FILM DESIGN

The thin film design which may be a candidate for the Hubble Space Telescope (HST) Wide Field Camera No. 3 is a UV-shifted durable silver high reflector. This design is based on work presented by J. Wolfe[15,16]. The design was modified to meet the optical and durability requirements for HST. The coating must meet the following optical specifications for one channel in the HST WFC3:

$R > 95\%$ $\quad 300\text{ nm} \leq \lambda \leq 1200\text{ nm}$

$R > 70\%$ $\quad \lambda = 200\text{ nm}$

The basic coating design is shown in Fig. 7. The materials for the enhancement layers are listed for three different coating designs: Phase I, II, and III. The Phase I design extends the high reflectance of silver down to 300 nm; Phase II shifts it down to 250 nm; and Phase III shifts down to 200 nm. The Phase III design meets the needs for the HST.



Phase	L	H
I	SiO_2	Ta_2O_5
II	SiO_2	HfO_2
III	SiO_2	HfO_2

Fig. 7 Coating design

The adhesion layer provides nucleation sites on the substrate for the sputtered silver , and works in combination with the NiCrN$_x$ layer to improve mechanical and chemical durability. The NiCrN$_x$ layer alloys with the silver and helps in preventing sulfides, chlorides and oxides from reacting with the silver. The silicon nitride layer improves mechanical durability and acts as a barrier layer preventing corrodants from reacting with the silver. The metal oxide layers are combinations of silica, tantala or hafnia and serve to increase the uv reflectance.

The essence of the uv-shifted durable silver coating is the thin silver layer on top of an aluminum layer and the encapsulation of the silver layer between two thin layers of nickel chrome nitride. Below about 380 nm, incident light is transmitted through the silver layer and reflected by the aluminum layer. Figure 8 compares Phase I, II and III to bare Ag.

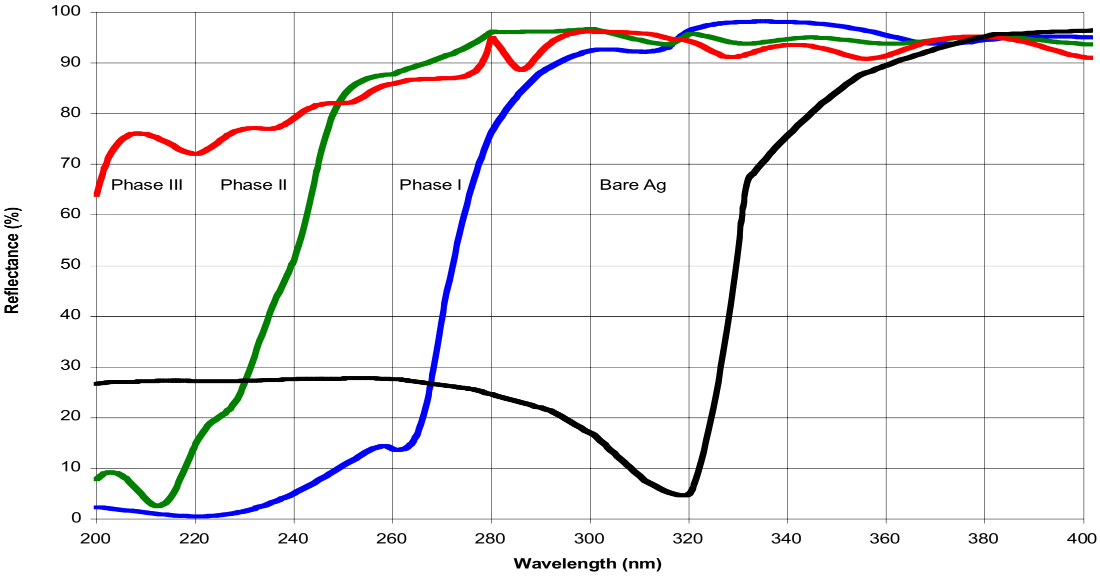


Fig. 8 Theoretical reflectance of Phase I, II, and III coating designs and bare silver.

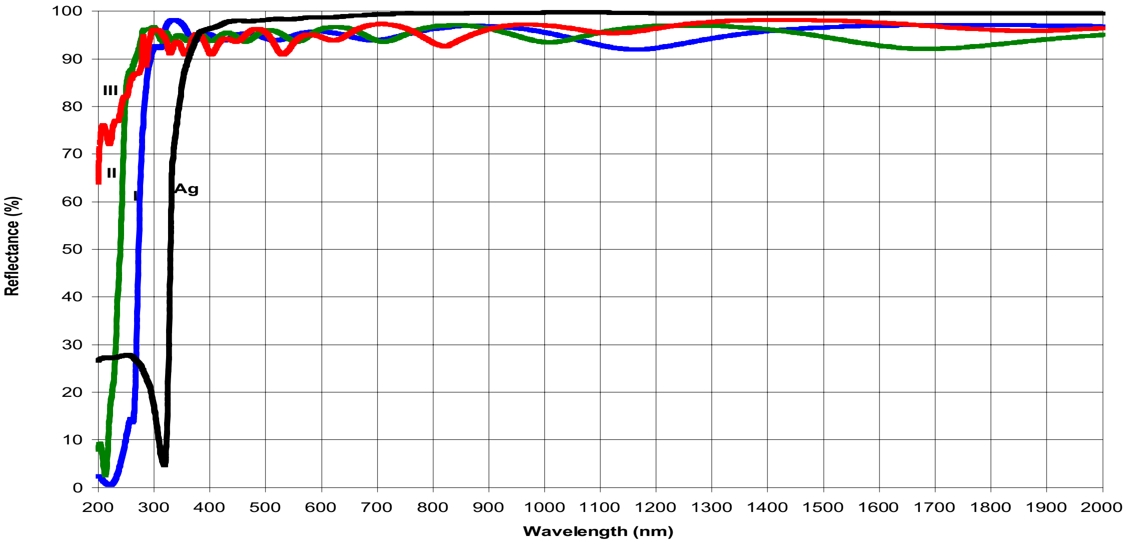


Fig. 9 Theoretical reflectance curves for Phase I, II and III designs compared to bare silver.

The silver layer also masks the dip in the aluminum at about 850 nm which is caused by inter-band transitions. Figure 8 shows the theoretical reflectance vs wavelength from 200 nm to 2000 nm for the Phase I, II and III designs and compares it to bare silver which is calculated from n and k obtained from Palik[23].

3. COATING RUNS

Early in the project, aluminum and stainless steel substrates were coated[8] using an Airco ILS-1600 sputter coater with a load-lock and DC magnetrons. This development was aimed at the National Ignition Facility where durable silver flashlamp reflectors were needed. Single layers of the various coating materials were coated onto separate aluminum substrates and characterized with a Woollam ellipsometer, Alpha Step profilometer, and Perkin Elmer Lambda 9 spectrophotometer. The adjusted design was coated onto diamond-paste polished aluminum substrates, stainless steel substrates, highly polished aluminum foil, and microscope slides overcoated with sputtered aluminum as a base layer. The coated microscope slides were scanned with a Perkin Elmer Lambda 9 spectrophotometer with an absolute reflectance attachment. The measured specular reflectance agrees to within 1% of the theoretical prediction. Several highly polished aluminum foils 0.030 inch thick and highly polished stainless steel 0.029 inch thick substrates were also coated with the design which showed excellent results. The coated foils could be curved in one dimension without harming the coating.

The coating runs for astronomical mirrors was done in a 48” X 48” X 60” box coater with both e-beam and pulsed DC magnetron sputter sources. The substrates were mounted on a single-axis rotary coating fixture approximately 8-inches above the sources. The coated witness samples were scanned on a Cary 5 spectrophotometer with a reflectance attachment. Initially, single layers were coated, scanned and the R and T data was used to determine the optical constants, n and k. An ellipsometer was used to determine the n and k for the “tri-layer” consisting of the Ag layer sandwiched between two $NiCrN_x$ layers. The NiCrNx layers are so thin that it is almost impossible to accurately model the “tri-layer” from the properties of single layers.

The measured reflectance curve for the Phase I coating is shown in figure 10. There is a slight dip at 320 nm which is where the surface plasmon resonance occurs.

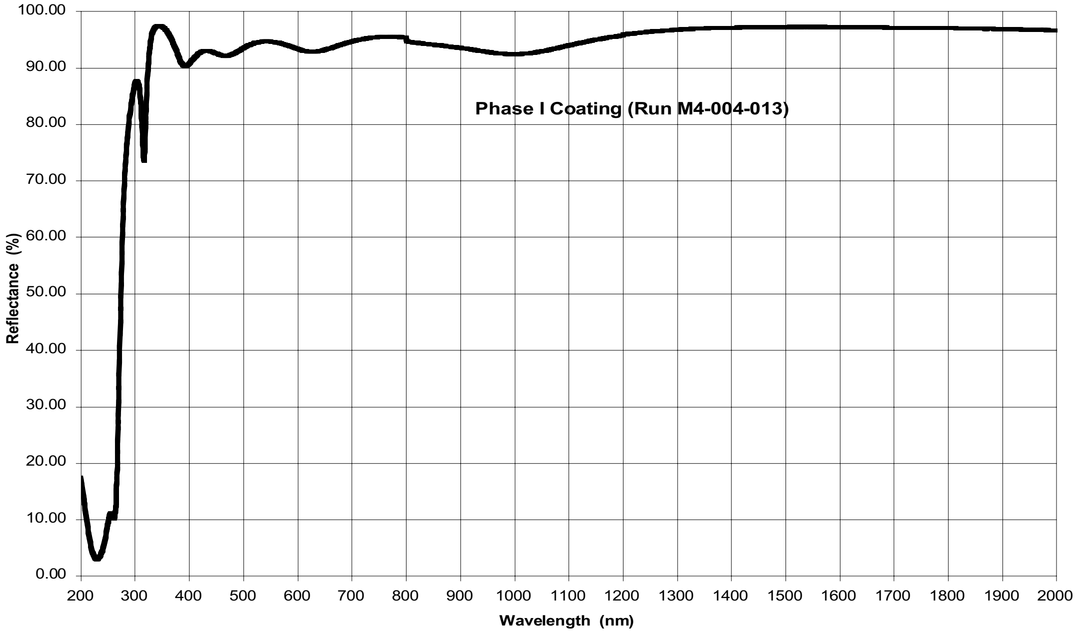


Fig. 10 Measured reflectance curve for Phase I coating

Although we did some work on the Phase II design, customer requirements demanded that we coat the Phase III design. The results are shown in figure 11 and are compared to the theoretical prediction.

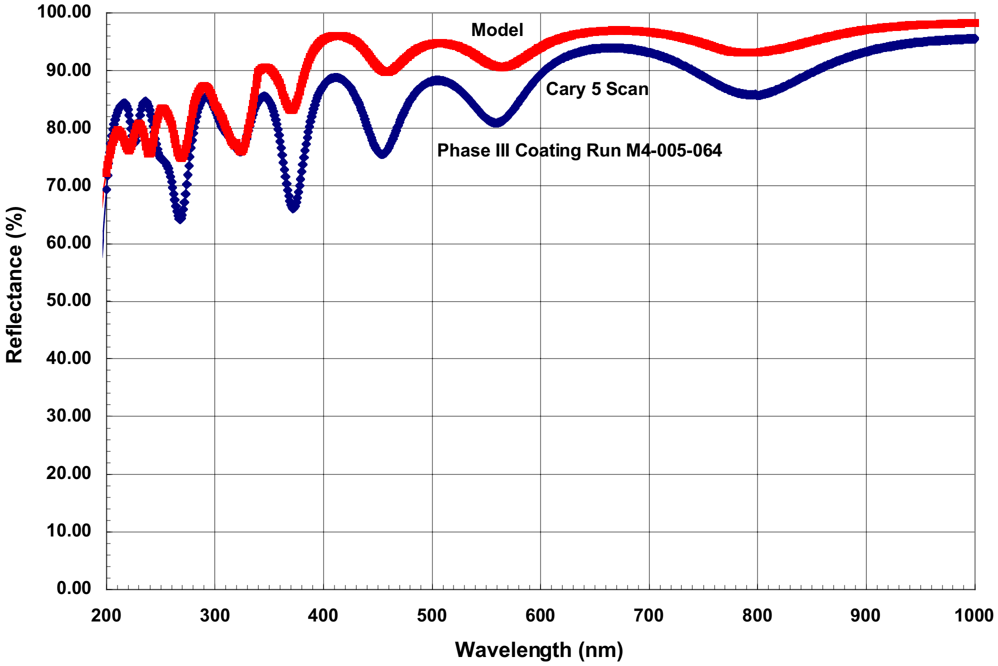


Figure 11 Early results of Phase III coating run compared to theoretical curve.

This coating did not meet the reflectance goal of 95%, however, the average reflectance at 200 nm was 80%. The uv optical constants of HfO_2 changed drastically with slight variations in the amount of activated oxygen in the plasma, therefore the optical thickness changed. This coating run showed that it is possible to extend the silver reflectance curve out to 200 nm where the average reflectance is 80%. Additional coating runs are being done in an attempt to boost the reflectance in the visible region.

4. ENVIRONMENTAL TEST RESULTS

Some of the coated parts were tested according to Mil Spec 13508C. They successfully passed tape, cheese cloth, and humidity. An additional test was performed in the flashlamp test facility where a coated aluminum sample was subjected to flashes from an intense flashlamp in a normal Livermore atmosphere with naturally-occurring corrodants. After two months testing and 20,717 flashes, there was no detectable change in reflectance of the protected silver. During the same test, bare silver mirrors corroded and either peeled off the substrates or developed a haze on the silver which was probably due to the growth of Ag_2S micro-crystals. Some other over-coated silver mirrors also failed the test.

The reflectance of the successful protected silver mirror before and after exposure is shown in Fig. 12. The latter sample was coated two years ago and was not a uv-shifted silver coating with an aluminum layer under the “tri-layer”, however, these curves demonstrated the durability of the silver “tri-layer” under intense flashlamp exposure. The reflectance curves before and after exposure lie on top of one another to within 1%, the accuracy of the measurement. A diamond scribe was used to scratch through the top coating layers which were exposed to normal atmosphere without any apparent corrosion.

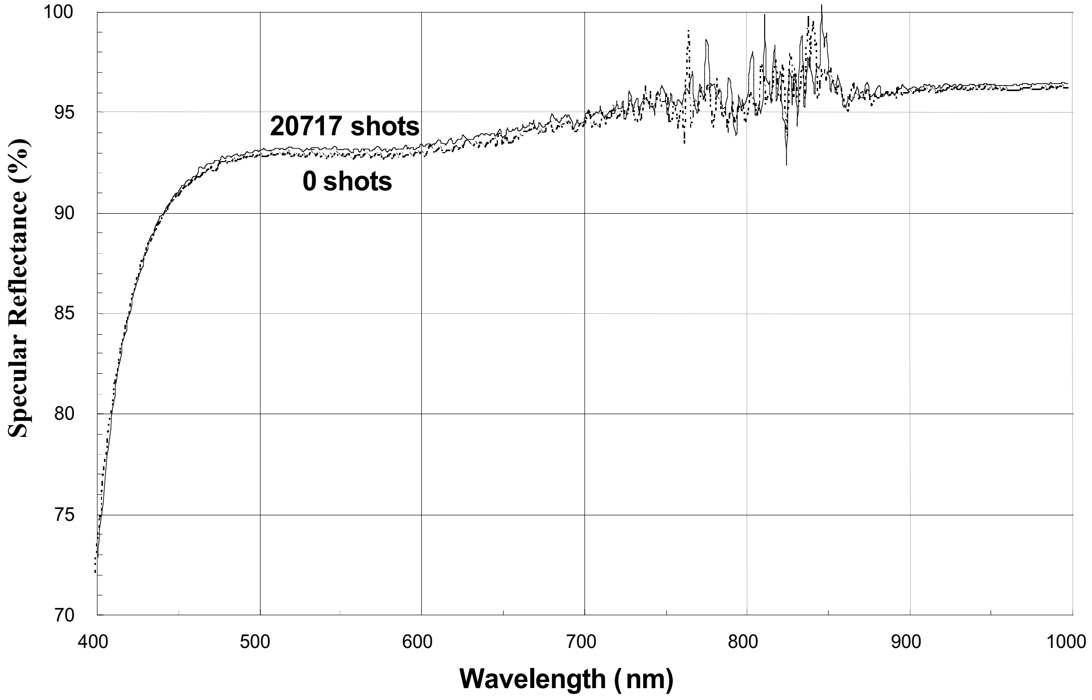


Fig. 12 Reflectance of protected silver mirror before and after 20,717 flashes and 2 months in a corrosive atmosphere.

5. COATING REMOVAL

We tried to remove the silver coating with several chemical solutions without success. A coated part was boiled in 1% salt solution for one hour without any apparent visual change. When one pint of Chlorox was added to the one gallon of boiling brine, the coating disappeared within ten minutes. We did not have time to pursue this development further.

6. FUTURE DEVELOPMENT

The future development of protected silver coatings for mirrors may include extending the reflectance down to 190 nm. An initial coating design shows promise in achieving this goal. We are working towards the goal of preventing tarnishing for at least 30 years under normal atmospheric conditions. We are also seeking a simple method to strip these durable silver coatings from the substrate. Although boiling brine and Clorox was shown to strip the coating, more development needs to be done to determine the optimum concentrations and times for this method.

7. CONCLUSIONS

A uv-shifted durable silver coating was designed and coated on both glass and metal substrates, including aluminum foil. This Phase I coating meets the optical performance specifications required for ground-based telescopes and extends the observing window down to 300 nm for silver coatings. The Phase III coating was shown to extend the high reflectance of silver down to 200 nm (R ≈ 80%), however, the reflectance above 400 nm was below the predicted value. Initial testing according to mil-spec 13508C indicates that this coating has the mechanical and chemical durability required for astronomical mirrors. Accelerated testing under flashlamp irradiation while in a corrosive environment showed that this coating probably has a 30-year lifetime in normal corrosive atmospheres. The results indicate that this uv-shifted durable silver coating may also be a good candidate for solar collectors located in the desert, and military instruments, in addition to ground-based and space-based astronomical telescope mirrors. The only chemical solution found to remove this coating was boiling salt, water and Clorox which removed the coating in ten minutes.

8. ACKNOWLEDGMENT

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