KRYPTON FLUORIDE LASER MIRROR STUDY

Final Report

for the period

October 1978 to November 1979

MASTER

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December 1979

Work performed under Contract No. DE-AC08-78DP40001
for the US Department of Energy
Division of Laser Fusion
Advanced Laser Program Office

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Printed in the United States of America

Available from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy \$4.50

Microfiche \$3.00

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Introduction

Rare gas halide lasers at 193 and 248nm will require lower-loss optics if mirrors and windows are not to be limiting factors in advanced DoE applications in laser fusion and photochemistry. The current commercial mirror technology must be improved, if higher damage thresholds and reliable UV laser operation are to be obtained.

This project addresses this problem in a number of ways, including materials investigations, test coatings, and fabrication of new UV laser coating designs, as described in more detail in the previous quarterly reports. Described in the final report are the process of making UV laser mirrors and the experimental strategy for attempting to improve them. Materials research is essential, and included selection and deposition of several candidate materials and an approximate ranking of their optical properties, so that new material combinations could be chosen, computer simulated, and deposited using improved vacuum techniques.

Analysis of the electric fields within a laser mirror were employed to lower coating loss. Enhanced metallic coatings may offer some advantages, although little is known about their damage threshold. A summary of test data is included, along with remarks on the survivability of UV laser optics, and possible future areas of inquiry, if truly low-loss UV laser mirrors are to ever be developed.

Experimental Applications of UV Laser Coatings

Ultraviolet laser mirrors play a small but vital part in a number of advanced laser experiments. At the recent Advanced Laser Program Review Meeting, several speakers described UV laser systems which operate at or near the fluence limits of current coatings and windows.

The rare-gas halide lasers are attractive as photolytic drivers for possible fusion lasers at longer wavelengths. Raman shifting and pulse stacking of KrF laser radiation is an area of intense current interest. Both types of experiments require efficient low-loss maximum reflectance coatings, both for normal and 45° incidence, as well as dichroic mirrors with maximum transmission at the pump wavelength. These dichroic mirrors are more difficult to fabricate to precise tolerances than conventional single-wavelength mirrors.

EXPERIMENTAL APPLICATIONS OF UV LASER COATINGS

**RESONATOR MIRRORS
STABLE AND UNSTABLE
FULL AND PARTIAL REFLECTORS**

**DICHROIC MIRRORS
KRF RAMAN SHIFTING
XEF & ARF DICHROICS**

**TURNING MIRRORS AND BEAM
INTEGRATORS**

**ANTI-REFLECTION COATINGS
PARTIAL REFLECTORS
WINDOWS AND LENSES**

Conventional stable resonators require partially transmitting coatings as well as maximum reflectors, and anti-reflection coatings. Unstable resonator designs generally utilize full reflector coatings only, although there are other types.

Beam Turning mirrors require coatings with maximum reflectance at 45° incidence. At the present time, it is possible to achieve reflectances within 1 to 2% of the best normal incidence reflectors, but KrF reflectors with more than 99% reflectance at 45° will require considerable development.

Ultraviolet Laser Mirror Process

UV laser mirrors are made analogously to visible and infrared mirrors, but due to materials limitations, special measures must be taken to minimize coating losses. For transmitting optics, substrate selection is limited to optical materials with bandgaps of at least 6eV, and preferably higher, which restricts the choices to silica, sapphire, and the fluorides of Mg, Ca, Ba, and Sr.

Metallic or ceramic substrates, if sufficiently well polished, can offer thermal advantages and may be of interest, for full reflectors in continuously pulsed lasers.

Materials selection for coatings involves choosing pairs of dielectric materials with the maximum refractive index difference and the lowest combined absorption. A greater choice of materials for coatings is due to the fact that several potential UV window materials have not been grown as larger crystals, but are available in the form of chunks.

Coating designs for laser mirrors have normally been classical quarterwave stacks, with alternating high and low index layers. Computer simulation methods are used to evaluate the projected reflectance, transmission, and absorption of multilayer coatings without incurring the expense of actual deposition and measurement; in this way the effects of different material combinations and possible design improvements can be evaluated without taking up expensive time in the coating chamber. When a coating design is optimized on the computer, actual deposition is performed by electron-beam heating of the coating materials in stainless steel chambers at high vacuum.

Optical testing of deposited coatings consists of direct reflectance and transmission measurements on each laser mirror.

ULTRAVIOLET LASER MIRROR PROCESS FLOWCHART

Research coatings are tested with a multiple-bounce reflectometer for greater accuracy. The results of reflectance and transmission testing are critical to the evaluation of possible coating improvements, as well as the day-to-day production of high performance UV laser mirrors.

Close visual inspection is necessary within the clear aperture of coated laser optics. Small substrate defects would tend to lower the resultant mirror's damage resistance, which indicates the importance of using a Nomarski interference contrast microscope in optical surface observations.

The effectiveness of these measures is determined by the results obtained in actual laser use. Although it is not always possible to determine conclusively the damage resistance of a coating, or guarantee its performance before new higher-power lasers are equipped with such mirrors, feedback from laser experimenters in the form of damage observations is extremely helpful in making such projections, and may well influence the choice of materials and coating designs. In cases of damage, sending laser mirrors back to the fabricator for examination and possible remeasurements can provide information in designing stronger optics.

Experimental Plan - KrF Laser Mirror Study

For this study, a number of well-polished substrates of UV grade fused silica were obtained. Baseline coatings at 2484A (97.7% measured reflectance) were typical of the current commercial technology, i.e. 97 to 98% R. Succeeding coatings were measured with respect to this coating, for possible improvements.

A number of high-bandgap materials were researched for potential use as coating materials, as shown on the next table, and for their availability in a form suitable for optical coating. Single-layer test coatings of several were deposited, as a means of judging their relative losses and approximate optical constants; improved vacuum levels during test coatings were achieved with additional trapping and cryopumping to reduce water contamination.

EXPERIMENTAL PLAN - KRF LASER MIRROR STUDY

TEST SUBSTRATES
BASELINE COATING
NEW MATERIALS RESEARCH
SINGLE-LAYER TEST COATINGS
IMPROVED VACUUM DEPOSITION
TECHNIQUES
NEW MATERIAL COMBINATIONS AND
COATING DESIGNS
ELECTRIC FIELD SIMULATIONS
MULTILAYER COATINGS
(QWOT AND NON-QUARTER WAVE)
ENHANCED ALUMINUM COATINGS
MATERIAL PURITY INVESTIGATION
FINAL REPORT AND RECOMMENDATIONS

On the basis of single-layer coating data, a number of new material combinations were selected, and evaluated for possible improvements to the existing state of the art. The standing-wave E-Field distribution within coatings due to laser irradiation was modeled, both for classical quarterwave stacks and designs with modified upper layers and lower losses, which may offer improved damage resistance.

Multilayer coatings of several types were deposited for comparison with baseline coatings, as were a few enhanced aluminum designs using the lowest-loss coating materials found.

Since the purity of the starting materials is felt to be an important contributing factor in UV mirror losses, an attempt was made using a commercial analytical service to determine the amount of impurities in three selected materials, for possible correlations with observed absorption losses.

A summary of data from baseline and test coatings is contained in this final report, as well as findings of materials investigations, and recommendations for producing better UV laser mirrors.

Baseline Coating Data

In order to establish a benchmark by which to judge future and possibly improved coatings, the proprietary ARC #248/FR coating, composed of a multi-layer using the proprietary ARC "L" and "H" materials, was deposited on fused silica substrates and measured for reflectance.

Tests at 2484A on this coating showed $97.7\% \pm 0.5\%$ reflectance, and less than 0.1% transmission. A multiple-reflection reflectometer and a new diffraction grating blazed for 2500A contributed to the improved accuracy of this and subsequent measurements.

Substrate Procurement

For test and final coatings, thirty-one inch diameter laser mirror substrates of UV grade fused silica were obtained. Single layer coatings were deposited on an additional group of 24 fused silica and 6 MgF_2 windows. For the $\frac{1}{4}$ " thick substrates in the first group, typical 2484A measurements were 90% T and 3.9% R. A typical Nemarski photomicrograph of an uncoated substrate surface was shown in the Second Progress Report under this contract.

Candidate Materials for UV Laser Coatings

It is desirable to have at least two low-loss dielectric materials with the greatest possible index difference. However, the general correlation found between high bandgap and low index implies that high-index materials must be used closer to their absorption edge, and can be expected to have lower damage thresholds than low-index materials.

Possible UV laser coating materials included fused silica, and the oxides and fluorides of Aluminum and the alkaline and rare-earth elements. Most alkali halides and alkaline-earth oxides absorb moisture readily, and were not considered practical. However recent reports indicate that NaF has a high threshold, despite its tendency to form easily fogged films, so it was included. Samples of high-purity NaF were obtained with the cooperation of Dr. Phillip Klein of NRL, near the end of the project.

Some good UV window materials such as CaF_2 and BaF_2 form very grainy films, which scatter far too much light to be useful, and were not included among the candidates for UV laser coatings. Other high bandgap fluorides including SrF_2 were evaluated as low loss materials, while rare earth oxides and fluorides (especially NdF_3 , Sc_2O_3 , and PrF_3) were explored for possible use as high index materials for new coatings.

In most cases a limited amount of impurity information was available from material suppliers, although an attempt was made to use the purest commercially available samples. Most commonly mentioned impurities were Ca, Fe, Mg, and Si, but potentially troublesome impurities (rare earths, transition metals, water content) are not routinely analyzed by the material manufacturers.

Single-layer coating data was used to make a preliminary selection of promising coating materials for new multilayer and enhanced Aluminum laser mirror designs; if the data were available, laser damage threshold rankings of the materials at the KrF and ArF wavelengths would have been extremely helpful, but no such studies have been reported.

CANDIDATE MATERIALS FOR UV LASER COATINGS

MATERIAL	APPROX. BANDGAP(Ev)	CUTOFF WAVELENGTH (A)
MgF ₂	11.0	1150
LiYF ₄	10.5	1185
NaF	10	1230
SrF ₂	9.6-9.7	1280
LaF ₃	9.7	1280
AlF ₃	9	1300-1350
Al ₂ O ₃	8.75	1450
SiO ₂ (crystalline)	8.4-8.7	1475
SiO ₂ (fused)	8.0-8.3	1600
NdF ₃	5.6-6.4	2000
Sc ₂ O ₃	6	2000
PrF ₃	5.9	2000

PLUS PROPRIETARY ARC H AND L MATERIALS.

Ranking of UV Laser Coating Materials

Most materials available for UV coatings have low refractive index ($n = 1.4$ to 1.6).. Low-loss materials explored for this project include MgF_2 , NaF , and SrF_2 as low index materials, as well as the proprietary ARC L material. Possible middle-index materials found to have low losses include NdF_3 and SiO_2 . The best new high-index material found so far is Sc_2O_3 , which is extremely costly but offers a good combination of high index and relatively low losses; Sc_2O_3 was employed in several of the new multilayer coatings done for this project, with good results.

KrF coating materials have extinction coefficients of about 1×10^{-3} for low materials and 3×10^{-3} for high materials. The following table shows the approximate "N" and "K" values of new materials; the emergence of high materials with less than 10^{-3} , or of low materials with a K value in the mid- 10^{-4} range would allow significant improvements in mirror coatings.

Although no materials with very low index were found to be superior to the proprietary ARC L material, low losses were observed for middle-index materials (SiO_2 and NdF_3). These may offer some absorption reductions when used in the outermost coating layers, but no multilayer composed of materials with a small index difference ($n_H - n_L = 0.20$ or less) can be made without danger of stress cracking, due to the number of layers required.

RANKING OF UV LASER COATING MATERIALS (BY APPROXIMATE OPTICAL CONSTANTS)

Improved Vacuum Deposition Techniques

Contaminants introduced to the substrate before and during the coating process may be a major contribution to UV coating losses. It was found in a previous Vacuum UV Laser Mirror Study that the addition of Liquid Nitrogen cold trapping to the standard coating procedure had beneficial effects; together with newly-cleaned chamber and fixtures, this enabled about 1.6% coating loss reduction at 1460Å. While absorption is not so great at 1930Å and 2484Å, further improvements in coating techniques may still be expected to reduce losses.

Efforts were made to improve coating techniques in several areas. A Torr Vacuum Products coaxial foreline trap was installed in the pumping line prior to the start of the final test coatings. A cryogenic pumping baffle was designed and constructed and was located in close proximity to the substrate during the coating cycle. This "cold plate" system should further reduce the amount of water vapor in deposited films, and was used during the deposition of some of the high reflectance coatings. A Hot Filament Ionization Gauge was installed in the evaporation chamber prior to starting test coatings, for more accurate pressure readings.

Substrate heating was increased to about 150°C during some of the final coatings; the necessary modifications to existing heating capabilities were completed during the third quarter.

New Material Combinations and Coating Designs

On the basis of single-layer coating data, promising materials for further investigation in their present forms included MgF_2 , SiO_2 , NdF_3 , ZrO_2 , Sc_2O_3 , Al_2O_3 , and the proprietary ARC "L" and "H" materials. A number of multilayer combinations were tried on the ARC PDP-11/03 computer, with the object of maximizing the index difference ($n_H - n_L$) and the minimizing the total absorption, as represented by the quantity ($k_H + k_L$). The best simulated MLD coatings showed 98-98½% reflectance at 2484Å; on the same basis a simulation of the ARC proprietary coating predicted 98.6% R, while 97.7% was actually measured.

In addition to the proprietary ARC "H" material, the most promising high-index materials selected for further testing were NdF_3 , ZrO_2 , and Sc_2O_3 ; these were all combined with the proprietary ARC "L" material, with results as indicated in the next table. The highest reflectivity and lowest loss was achieved with NdF_3 , although because of its relatively low index many layers were required—signs of stress cracking were observed after deposition. The small refractive index difference between NdF_3 and "L" resulted in a very narrow spectral region of high reflectance, which increases the difficulty of monitoring of the coating's peak wavelength, and the fabrication of future laser mirrors with this coating to precise wavelength tolerances.

When NaF was substituted as the low-index material and paired with Sc_2O_3 , the measured reflectivity and loss worsened by about 1-3/4%.

New Multilayer Coating Combinations and Test Results

<u>Run #</u>	<u>High Index Material</u>	<u>Low Index Material</u>	<u>Design</u>	<u>Results:</u>		
				<u>%R</u>	<u>%T</u>	<u>Loss(%)</u>
1250*	NdF ₃	L	H(LH) ¹⁷	98.1	1.1	0.8
1253	NdF ₃	L	H(LH) ¹⁷	97.7	0.7	1.6
1207	ZrO ₂	L	(LH) ¹⁰	97.5	0.2	2.3
1252	Sc ₂ O ₃	L	H(LH) ¹³	97.3	0.1	2.6
1247	Sc ₂ O ₃	NaF	H(LH) ¹³	95.6	0	4.4

All coatings are quarterwave stacks

R. and T. values are for 2484A, except Run #1253, which peaked at 2537A.

L = ARC proprietary low-index material

*Substrate heating employed on Run 1250, but not on Run 1253

Enhanced Metallic Coatings

The only practical metallic reflecting film at 1933A and 2484A is Aluminum. Unprotected Al films quickly form a UV-absorbing oxide overcoating, upon exposure to the atmosphere. To preserve far UV reflectance at 1933A especially, protective overcoatings of MgF_2 have been applied, in a process developed by Georg Hass and others in the late 1950's^{1,2}. However, the reflectance of such a broadband coating (Al + approx 400-500A MgF_2) is only 88-90% at 1933A, and 1-2% higher at 2484A. Due to its absorption losses, this type of coating on silica or fluoride substrates is unlikely to be suited for high power UV lasers.

Although Aluminum is the most highly reflecting metal in the UV, current MgF_2 overcoated Aluminum films can be expected to damage readily at vacuum UV laser wavelengths, at fluences much over a few tenths of a joule/cm². The best 1720A dielectric mirrors may be capable of 50 shots at approx 1/2J/cm². The absorption-induced heating of the Al layer caused the melting and evaporation of the films shown by MSNW at the recent DoE Advanced Lasers Meeting, because the heat could not rapidly diffuse away from the beam spot.

There are two ways of attacking this problem, if Aluminum coatings are to be used. One is to improve the thermal conductivity of the substrate. Several years ago, Wallace and Dreyfus of IBM theorized that increased performance would be obtained from Al- MgF_2 coatings when Sapphire was used as a substrate material. However the coating absorption was such (15%) that damage thresholds would not be high enough for the recent Xenon and Krypton laser experiments at SRI, AVCO, and MSNW.

- 1) Hass, G. and R. Tousey, JOSA vol 49, p.593 (1959)
- 2) Angel, D.W., et. al., JOSA vol 51, p.913 (1961)

A second way to make a possibly more resistant Al-coated mirror is to enhance its reflectivity at the laser wavelength with an abbreviated multilayer dielectric coating. When such coatings were simulated, they exhibited theoretical reflectances slightly lower than full MLD "stacks" but they showed about 75% reflectance in the visible, which can be useful for alignment purposes.

While no comparison of damage behavior is yet possible with all-dielectric coatings, three multilayer-enhanced Al coatings were designed and fabricated; the best results (97.5% R @ 2484A) were achieved when a modified ARC #248/TR proprietary coating was added to a layer of approx. 2000A of Al.

Coating performance in the spectral range of the ArF laser (Runs 339 and 340) was no better than a good Al-MgF₂ coating, and further work in this area will be needed to extend enhanced Aluminum coatings into the vacuum ultraviolet region.

Enhanced Aluminum Coating Results

<u>Run #</u>	<u>High Index Material</u>	<u>Low Index Material</u>	<u>Design</u>	<u>Results</u>
338	H	L	Al+(LH) ⁶	97.5% R @ 2484A
339	NdF ₃	L	Al+H(LH) ⁵	97% R @ 2650A peak; 92% R @ 2484A 89% R @ 1950A peak; 85% R @ 1933A
340	SiO ₂	L	Al+(LH) ⁶	95% R @ 2600A peak; 92% R @ 2484A 90% R @ 1950A peak; 87% R @ 1933A

-all dielectric layers were one quarter-wave thick

Electric Field Distribution Within Laser Coatings

In a two-material multilayer coating with all layers one quarter wavelength thick, the highest fields are found at the "high-to-low" layer interfaces, while nodes of the standing wave pattern occur at "low-to-high" interfaces, as indicated on the next figure.

Since the high index material generally has the higher absorption and lower damage thresholds, the peak internal fields and total power dissipation in the coating due to absorption may be lowered by reducing the thickness of the H layers. In practice only the top few layer pairs have much effect. In an all-QWOT stack each layer's optical thickness is $\frac{1}{4}$ wave, and the basic period is one half wave thick. This basic period is not maintained exactly in the non-quarterwave design approach, as the total thickness of the added (HL) pairs is generally not a half wave. Although higher damage thresholds are not assured and could only be verified by comparative laser damage testing, this method should result in lower absorption losses due to standing wave fields, as first pointed out by Gary DeBell in his thesis at Rochester.

For this method to result in improved mirror resistance to damage, pulse lengths should be short, and the coatings relatively free of absorption and defects that could cause failure at lower levels for reasons other than dielectric breakdown, according to the analyses of Newnam and Gill. The relative damage thresholds of the constituent low and high index materials must be known as well; however in any case, the same procedure can be used to minimize the coating loss in the uppermost layers, which depends only on the optical properties and the time-averaged field intensity for each layer.

The E-field analysis/NQW design method was applied to several all-dielectric and enhanced aluminum designs, of which the most promising were fabricated, using a modified monitoring system to produce the non-quarterwave layers required.

As indicated in the accompanying Table, the best NQW coatings resulted in measured reflectances of about 98%, with the combination of NdF_3 and the proprietary low-index material having the lowest loss (about 1.4%). A modification of the proprietary ARC 248/FR coating (Run 1257) consisted of replacing the "H" material in the top few layers with NdF_3 ; an improvement in loss of 0.6% relative to the all-QWOT baseline coating was observed. It should be kept in mind, however, that this apparent loss reduction is of the same order as the $\pm 1/2\%$ estimated uncertainty in the reflectance measurements.

Non-quarterwave MLD Coatings and Test Results

<u>Run #</u>	<u>High Index Material</u>	<u>Low Index Material</u>	<u>Design</u>	<u>Results:</u>		
				<u>%R</u>	<u>%T</u>	<u>Loss(%)</u>
1254*	NdF_3	L	$\text{H}(\text{LH})^{14}(\text{LH})_N^2$	98.1	1.4	0.5
1257	H ($\text{H}_2=\text{NdF}_3$)	L	$(\text{LH})^7\text{LH}_2(\text{LH}_2)_N^2$	98.0	0.3	1.7
1255	Sc_2O_3	L	$\text{H}(\text{LH})^{11}(\text{LH})_N^2$	98.1	0	1.9

L = ARC proprietary low-index material

H = ARC proprietary high-index material

* Run 1254 peaked at 2537Å

Subscript "N" indicates non-quarterwave layer pairs

"NORMALIZED STANDING WAVE ELECTRIC FIELD INTENSITY" in-between Layers 16 to 21,
(Counting from the Substrate). TOTAL Design PHYSICAL Thickness = 800.25 nm
=====

Electric Field Simulation #1: Typical multilayer quarterwave stack, evaluated for reflectance, transmission, absorption, and standing-wave electric field intensity ($\bar{E}^2$), within top 6 layers of coating design of the form H(LH)¹⁰. Note that E field intensity is zero at the surface, and at all "Low-to-High" interfaces. E-field peak occurs at the bottom of the top H layer.

"NORMALIZED STANDING WAVE ELECTRIC FIELD INTENSITY" in-between Layers 1 to 21,
(Counting from the Substrate). | TOTAL Design PHYSICAL Thickness = 813.82 nm
=====

"r" [4] is Percent ==>> 90.0000 92.0000 94.0000 96.0000 98.0000 100.000
"e" [3] is $E^2(A)^2$ ==>> 0.0000 0.5000 1.0000 1.5000 2.0000 2.500

Electric Field Simulation #2: Same design as previous simulation, except the top two layer pairs have been adjusted so that the H layers are 1/8 wave thick while the L layers are 3/8 wave thick at 250nm. The E-field peak now resides in the L layer, which has lower absorption. Coating shows approximately 0.2% more R, 0.1% more T, and 0.3% less A, with respect to same design using all QWOT's.

Material Purity Study

It has been observed that thin films of most coating materials have approximately 10,000 times the absorption of the best bulk crystals. Some of this absorption is no doubt due to impurities in the starting materials. For this reason, the purest available coating materials were used in an attempt to make the lowest-loss UV laser coatings, and effects of material purity were further investigated. Based on initial single layer tests, two of the lowest-loss coating materials were analyzed for impurity content. For comparison, a promising material with significant absorption was analyzed. Availability of higher purity forms of the selected materials were investigated.

For single-layer test coatings, the purest commercially available materials were used; typically the material manufacturer supplied only a "lot analysis" which included maximum detection limits of a partial set of the elements. Since sub-ppm concentration of some elements (e.g. rare earths and transition metals) may cause significant UV absorption, the standard impurity testing procedures do not give enough information to evaluate the effects of impurities on coating losses. The most frequently cited impurities in the manufacturers lot analysis reports, were Calcium, Magnesium, Iron, and Silicon, with detection limits varying from 50 to 500 ppm. Metals such as Aluminum, Chromium, and Manganese may be present in lesser concentrations. In the case of the rare-earth compounds, contamination with other rare earths is unfortunately likely, and difficult to prevent or detect.

When each material was purchased, the supplier was questioned as to whether it represented the purest available form, and whether a purer version was available.

The manufacturers were of the consensus that purer materials could not be made on a commercial basis at a reasonable cost, but if troublesome impurities are known in specific instances, it may be possible to make improvements. However, the chemical analysis data available from the manufacturers is incomplete at best, considering that

their materials have nominal total impurity levels of only 1 to 100 parts per million, and further testing of starting materials was felt to be necessary.

One facet of this project was to analyze at least three materials (determined on the basis of single-layer test coatings) for impurities. Two of the most promising low-loss materials (NdF_3 and Sc_2O_3) were chosen, along with a promising material (NaF) which exhibited higher film absorption than its bandgap might suggest. The information obtained was used to correlate the presence of impurities with UV absorption, and to indicate whether purer starting materials were necessary. Two types of MgF_2 samples, UV grade crystal chunks and coarse powder, were also compared in the same way.

The services of an analytical testing company were required for material impurity analyses. The United States Testing Company tested ARC-supplied coating material samples by optical emission spectroscopy and X-ray fluorescence; their results on ARC-supplied samples of NdF_3 , Sc_2O_3 , NaF , and two types of MgF_2 are reproduced as an appendix to this report. The NdF_3 sample showed no detectable impurities, which correlates with the fact that it had the lowest single-layer loss figures of all materials deposited. Sc_2O_3 showed faint traces of Boron and Magnesium (less than 100 ppm) which appear to have little effect, if any, on the observed absorption; however, their presence indicates it may be possible to further refine the material in the future. The Sodium Fluoride sample showed faint traces of Copper and Magnesium, but not enough to explain the large losses observed upon evaporation; a more likely cause is the hygroscopic nature of NaF , which causes it to form poor films. Both MgF_2 samples showed the presence of Silicon; the small chunks from a laboratory supply house showed much more Si impurities than the fractured UV grade single crystals.

Survivability of UV Laser Optics

A complete discussion of the factors which determine the lifetime of laser mirrors in actual use and in future advanced laser program applications would include several areas beyond the scope of the study. Shorter wavelength lasers have lowered efficiencies, due to losses in the optics and photoabsorption in the laser medium. Several technical problems cause current UV excimer lasers to be limited by optical constraints; important to the development of larger and more efficient UV laser systems is further progress toward mirrors and windows which can withstand high peak and average power levels. Long-term survival of UV laser optics and windows is an area in which little research has been done, although ARC KrF turning mirrors have survived over ten million pulses at LLL (private communication with Dr. John Murray).

Systematic laser damage testing at 2484Å has not been reported, although damage for single pulses may occur at fluences of 3-5 J/cm² for 1/2-1 microsecond pulses, and 1-3 J/cm² for pulses a few tens of nanoseconds long. Damage thresholds decrease at shorter wavelengths, and are likely to be less than 1 J/cm² in the vacuum UV even for current dielectric coatings. Newnam observed an approximate correlation between damage threshold and the square of the laser wavelength, on the basis of tests at 266 and 355nm; on this basis one might expect ArF coating thresholds to be about 60% of those for KrF mirrors.

F₂ exposure effects on coatings are of practical importance, but their study is beyond the project's authorized tasks. The highest resistance to Fluorine appears to be found with solid windows of MgF₂ and CaF₂, which a thin film coating would be hard pressed to duplicate. On a limited basis the lifetime of internal cavity mirrors can be improved with protective overcoatings; however, this does not seem to offer a long-term solution to the problem, and future research in this area is needed if internal cavity coated optics are to be used. Water vapor penetration of

laser cells should in any case be minimized, to prevent formation of HF or HCl, which will attack the optics.

A complete explanation of the behavior and failure modes of laser coatings in actual use also would include the thermal and mechanical properties of the coating materials, with respect to the substrate used in each case; and film adhesion studies. The available data is incomplete, especially with regard to new materials of current interest such as LiYF_4 , so it is not yet possible to make a relative comparison of all the materials under consideration, apart from ranking them by approximate optical constants.

Temperature-induced absorption in Aluminum coatings has been advanced as a possible cause of transient, reversible decreases in their reflectivity at sub-damage threshold levels (Dr. James Gerardo, private communication) which may be a contributing factor in premature pulse termination observed in VUV lasers by several experimenters. Premature termination of VUV laser pulses was reported by several speakers (Boness, Eckstrom, and Center) at the recent DoE Advanced Laser Program Review Meeting. Although the precise mechanism limiting the laser output is not known, it is possible that temperature-dependent absorption in the coating materials is one cause, as has been reported at longer wavelengths by several experimenters.

The maintenance of UV laser coatings in their initial uncontaminated state is important for maximum performance in single pulses, and especially for continuous pulsed operation. Unless a mirror is accidentally contaminated, all but the most careful attempts to clean the coating will probably make the situation worse, and cause more absorption at the coating surface. One possible solution is a rear-surface mirror, made by depositing a low-loss coating on the back side of an MgF_2

or CaF_2 lens or window which is suitably polished. There are at least three advantages---

1. Uncoated windows should have higher thresholds than coatings, and better F_2 resistance.
2. Reduced fields at substrate-coating interface, where damage might be expected in a rear-surface mirror.
3. Cleanliness of the substrate-coating interface, is maintained at its original level, reducing output degradation with time.

Although advanced lasers may have pulse rates up to 1 KHZ, very little information is available on the average-power limitations of UV laser mirrors. Certainly minimizing coating loss and Fluorine damage, and maintenance of coatings in a clean state, will be even more important than at present, and more attention must be given to the thermal properties of the coating-substrate combination.

RECOMMENDATIONS

- External mirrors last longer than internal
- Rear-surface optics may be best
- MgF_2 lasts longer than SiO_2 in contact with F_2 ; CaF_2 is also good.
- Testing of R and temperature of a mirror during a pulse to determine possible cause of premature pulse termination, with an instrument such as the LLL two-photon absorption spectrometer described by Dr. Lee Smith
- Cooperative damage threshold testing, and examination of damaged mirrors
- Design of UV laser systems for sub-threshold fluence; minimize beam diffraction and "hot spots"

Conclusions

Due to the importance of UV laser mirrors in current and future laser systems, an attempt was made to improve their performance in several ways. It was shown that the baseline coating reflectance of 97.7% was exceeded in several of the best test coatings, using the materials Sc_2O_3 and NdF_3 , and the proprietary ARC high and low index materials. With special measures including very pure starting materials, low chamber pressures, cryogenic cooling, substrate heating, and non-quarter-wave designs, it is possible to reduce KrF coating losses to $\frac{1}{2}$ to 1%. However, a reflector which has over 99% R at 2484A will still be difficult; the best coatings have a small amount of transmission because it is counterproductive to apply enough layers to completely extinguish their transmission.

The best quarterwave coating fabricated was a 35-layer coating employing NdF_3 and the ARC L material; measured performance was 98.1% R, 1.1% T, and 0.8% total loss (which includes both absorption and scattering losses) when the substrates were heated to about 150°C. This coating showed signs of stress cracking, however, and was very narrow in spectral width and difficult to fabricate.

Several non-quarterwave coatings were done, in an attempt to further reduce coating losses by making the upper two high-index layers thinner than a quarter wave because of their higher absorption. This had the effect of lowering the peak field intensity within the coating, and shifting it to the top low index layers, which have lower absorption.

Three such coating designs achieved reflectances of about 98%, with losses ranging from 0.5% to 1.9%. Although it was not possible to produce a mirror with more than 98.1% reflectance, loss reductions of 0.7% to 1.1% were achieved by these methods and it is assumed that laser mirrors thus coated will perform better in actual laser use. Any increase in damage thresholds would have to be verified experimentally.

Enhanced Aluminum coatings were attempted for the 2484A region, and also for the ArF laser wavelength. 97 to 97.5% reflectance was achieved at the peak of the two best coatings, the best being a modification of the proprietary ARC baseline coating. So it is possible in the best of situations to have an enhanced Al mirror with peak reflectance within 1/2 to 1% of the best KrF multilayer stacks, and about 75% reflectance in the visible. It remains to be seen, however what the damage behavior of this type of coating is.

At 1933A the measured reflectance of two types of enhanced Al coatings was 85 to 87%, although at 1950A 89 to 90% was achieved. Further work will be necessary to extend this technique down to 1933A, on the basis of the test coatings' results. Because of the lower refractive index difference between the materials available for use at 1933A, more layers will have to be used, and lower peak reflectances are to be expected.

Several materials of interest were found to have low absorption in the form of single thin film layers, including Sc_2O_3 , SiO_2 , NdF_3 , and the proprietary ARC H and L materials. Promising thin film coatings were done with Sc_2O_3 , NdF_3 , H, and L, with the combination of Sc_2O_3 and L giving the best combination of low loss and practicality. NaF tended to form poor films, and showed high losses in both single layers and multilayer coatings. Analyzed for chemical impurities were Sc_2O_3 , NdF_3 , NaF, and two types of MgF_2 ; the only material found to have no detectable impurities was NdF_3 , which also showed the lowest film loss. The NaF showed faint traces of Copper and Magnesium, but not enough to explain its high losses, which are more likely caused by the affinity of NaF for water vapor.

Recommendations

Possible areas of future research include development and chemical analysis of ultrapure materials, possibly with the cooperation of the Naval Research Laboratory and the MIT Crystal Physics Laboratory, and inquiries into the existence and availability of such possible Fluoride-analog materials as SiF_4 , ScF_3 , TiF_4 , ZrF_4 , YF_3 , and YAlF_3 .

Studies of film structure may serve to correlate any observed coating defects with film absorption and consequent damage behavior. Thin film adhesion to and interaction with candidate substrate materials merits further study, as well as the use of so-called "barrier layers" next to the substrate, which may strengthen AR coatings and partial reflectors, and the concept of protective outer layers. Controlled exposure of candidate window and film materials to HF and HCl would serve to prequalify those materials which may have the best resistance to the various rare gas halide laser media; however the cavity flux and any charged particles present will certainly also have deleterious effects on the exposed intracavity optical surfaces.

Reduction of chamber pressures to the 10^{-8} to 10^{-9} torr range may result in a lower level of film impurities and absorption, to the point where single-wavelength calorimetry will be necessary to more accurately measure coating losses in the 0.1 to 1.0% range. Further improvements in the accuracy of UV reflectance measurements would be necessary to distinguish between a 98% reflector and the elusive ideal of a 100% reflector; a reflectometer of a confocal design which utilized 10 to 20 reflections of similarly coated concave witness samples would allow more accurate distinctions of a few tenths of a percent R. A vacuum ellipsometer would be the best means to measure candidate materials' optical properties.

Cooperative damage thresholds testing of windows and films is long overdue at the excimer laser wavelengths, although Newnam and Smith have reported useful data

at the 3550A and 2660A harmonic wavelengths of the Nd: YAG laser. Systematic damage studies at 2484A, 1933A, and at vacuum UV laser wavelengths would be of great help in improving UV laser mirror technology.

Post-deposition treatment of coatings may offer advantages of better film properties, and for this reason thermal annealing and the feasibility of laser recrystallization of films merits consideration.

United States Testing Company, Inc.

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REPORT OF TEST

October 3, 1979

CLIENT: Acton Research Corp.
525 Main Street
Acton, MA 01720
Attn: Mr. L. Stelmack

NUMBER

68086

SUBJECT: Five samples:

1) NdF_3 -A

2) Sc_2O_3 -B

3) NaF -C

4) MgF_2 -D

5) MgF_2 -E

OCT - 5 1979

Authorization: P. O. #04704

PURPOSE & PROCEDURE:

Emission spectrographic metal scans of all samples and X-ray fluorescence scan of sample E (MgF_2 -E).

RESULTS:

The X-ray fluorescence scan of sample E (MgF_2) showed no detectable impurities. Any impurities would have had to be in the hundreds of ppm to be detectable.

The results of the semi-quantitative metals scans are attached and indicate the materials are pure. The only significant impurity was silicon at the minor level in sample E. In general, rare earth detection levels in rare earth materials by routine emission spectrography is 100 ppm, in the scandium salt about 50 ppm and in the magnesium salt about 10 ppm. Some rare earths are more sensitive than others. The ones reported are Y (Yttrium), Eu (Europium), Yb (Ytterbium), Lu (Lutetium) and Er (Erbium).

SIGNED FOR THE COMPANY

BY

Alan Schoffman

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jiw

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Acton Research Corp.

Sample Identification

1.	52 - A
2.	53 - B
3.	54 - C
4.	55 - D
5.	56 - E

Semi-quantitative Spectrographic Analysis

	1	2	3	4	5		1	2	3	4	5		1	2	3	4	5
Aluminum	ND	-	-	-	-	Magnesium	ND	ft	ft	P	P	Zinc	ND	-	-	-	-
Arsenic	ND	-	-	-	-	Manganese	ND	-	-	-	-	Zirconium	ND	-	-	-	-
Antimony	ND	-	-	-	-	Molybdenum	ND	-	-	-	-	Additional Results:					
Barium	ND	-	-	-	-	Niobium	ND	-	-	-	-						
Beryllium	ND	-	-	-	-	Nickel	ND	-	-	-	-		Nd	P	ND	-	-
Boron	ND	ft	ND	ND	ND	* Phosphorus	X	X	X	X	X		Sc	P	All	ND	
Bismuth	ND	-	-	-	-	* Potassium	X	X	X	X	X		Y		All	ND	
Cadmium	ND	-	-	-	-	Sodium	ND	ND	P	ND	ND	Eu			All	ND	
Calcium	ND	-	-	-	-	Silicon	ND	ND	ND	ft	m	Yb			All	ND	
Chromium	ND	-	-	-	-	Silver	ND	-	-	-	-	Lu			All	ND	
Cobalt	ND	-	-	-	-	Tantalum	ND	-	-	-	-	Er			All	ND	
Copper	ND	ND	ft	ND	ND	Tin	ND	-	-	-	-						
Iron	ND	ND	ND	ND	ND	Titanium	ND	-	-	-	-						
Lead	ND	-	-	-	-	Tungsten	ND	-	-	-	-						
Lithium	ND	-	-	-	-	Vanadium	ND	-	-	-	-						

P - 10 to 100%

M - 1 to 10%

m - .1 to 1.0%

t - .01 to .1%

ft - less than 0.01%

vft - very faint trace

H - Upper half of range shown

L - Lower half of range shown

ND - Not detected

X - Not tested

* Phosphorus and Potassium
only if P or M.

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