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Optical Interference Coatings
for the Infrared
Final Report
covering the period
February 1, 1978 to September 30, 1978
Research Contract EY-76-S-04-3583
Modification A004 with
U.S. Energy Research and Development
Administration
under auspices of group AP-2
Los Alamos Scientific Laboratory

Principal Investigator:
Philip Baumeister

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Principal Investigator: Philip Baumeister

The Institute of Optics

University of Rochester

Rochester, New York 14627

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A B S T R A C T

Several types of multilayer interference reflectors were produced: (a) With a high reflectance at $\lambda = 16 \mu\text{m}$ and high transmittance at $9.4 \mu\text{m}$; (b), High reflectance at $9.4 \mu\text{m}$ and high transmittance at $16 \mu\text{m}$; and, (c), A reflector at $\lambda = 11.3 \mu\text{m}$. The stacks were fabricated by evaporating alternate layers of ZnSe and PbF_2 in a vacuum.

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I. Introduction:

1.1 Objectives

As outlined in the work statement, the objectives are to "study the properties of multilayer anti-reflection coatings and multilayer reflectors in the infrared region of the electromagnetic radiation spectrum. Attempt shall be made to deposit multilayer anti-reflection coatings and multilayer reflectors that are transparent in the wavelength region near 16 micrometers. Zinc sulfide, calcium fluoride and lead fluoride shall be the initial choices for the materials."

In the fulfillment of these goals, we have deposited some successful ARC's that are described in a previous report.¹ This report focusses upon reflectors.

1.2 Reflectors

Three types of reflectors were considered. The first should have a substantial reflectance at $\lambda_0 = 16 \mu\text{m}$ and a high transmittance near $10 \mu\text{m}$. The second type should have the opposite characteristics: A high reflectance near $10 \mu\text{m}$ and relatively high transparency at $16 \mu\text{m}$. Another reflector was designed for use at $\lambda = 11.3 \mu\text{m}$.

The first two designs are used with an optically pumped laser -- where the pump is at $10 \mu\text{m}$ and the output is at $16 \mu\text{m}$. The reflector at $10 \mu\text{m}$ has several advantages over the $16 \mu\text{m}$ reflectors. First, the layers are much thinner and therefore the mechanical stress is not

as great. Another advantage is that the thinner layers do not absorb as much flux and have higher resistance to laser damage.

2 Stack Designs

As mentioned in 1.2, three types of stacks were designed. One was a dichroic with high reflectance at 16 μm and high transmittance at 10 μm . A second was dichroic with just the opposite characteristics, high reflectance at 10 μm and high transmittance at 16 μm . The third design was a reflector at 11.3 μm . Each design is discussed in turn.

2.1 16 μm Reflector Design

The dichroic with high reflectance at 16 μm consists of a stack with basic period:

$$\left(\frac{L}{2} \quad H \quad \frac{L}{2} \right)$$

where: L = Quarterwave optical thickness at 16 μm of low index material; and,

H = Quarterwave optical thickness at 16 μm of high index material.

This basic period is repeated several times to achieve high reflectance, as for example:

$$\left(\frac{L}{2} H \frac{L}{2} \right)^7 = \frac{L}{2} (H L)^6 H \frac{L}{2}$$

which may be viewed as a 15 layer stack consisting of 13 quarterwave layers sandwiched between two eightwave low index layers. The next step is to calculate the equivalent index of the basic period and to design an antireflection coating ARC that matches this equivalent index to the substrate on one side and air on the other, at the wavelength where high transmittance is desired.

It is fortuitous that the equivalent index of the PbF_2/ZnSe stack with quarter waves at $16 \mu\text{m}$ is close to unity at $10 \mu\text{m}$ so that it is automatically matched for air. Thus only a stack-substrate matching layer is required. A single layer ARC is designed by satisfying the square root condition, namely

$$N_{\text{film}} = \sqrt{(N_{\text{substrate}})(N_{\text{stack}})} \quad (1)$$

where: N_{stack} = stack equivalent index;

$N_{\text{substrate}}$ = substrate index; and,

N_{film} = film index.

For the case of a CdTe substrate, $n_{\text{film}} = 1.63$, which is serendipitously the index of PbF_2 at $10 \mu\text{m}$! When ZnSe substrates are used, an index of 1.55 is needed for the matching layer. However, this index of 1.55 is so close to the index of lead fluoride as to cause negligible reflection loss (<1%). The matching layer for this dichroic design consists of a quarterwave at $10 \mu\text{m}$ of PbF_2 . The design is now:

$$\text{Substrate}/L' \left(\frac{L}{2} \text{ H } \frac{L}{2} \right)^m / \text{air}$$

where $L' = \text{Quarterwave of } \text{PbF}_2 \text{ @ } 10 \mu\text{m};$

$m = \text{number of basic periods; and}$

L, H have the same meaning as above.

Since L' and $\frac{L}{2}$ are the same material, they coalesce into a single layer and the general design takes the form

$$\text{Substrate}/L'' \text{ H } (L \text{ H})^{m-1} \frac{L}{2} / \text{air}$$

where $L'' = L' + \frac{L}{2} = \text{Quarterwave @ } \lambda = 20 \mu\text{m} \text{ of } \text{PbF}_2$

2.2. Mechanical Stress

It was found that stress in the thin films caused peeling in the foregoing design when more than 7 layers were used. As described in the interim report,¹ ZnSe exhibits compressive stress while PbF_2 is tensile. By increasing the PbF_2 thickness and decreasing the ZnSe

thickness the stresses can be balanced against one another. It was found a 15% increase in PbF_2 thickness and a 15% decreased in ZnSe thickness accomplished this stress balancing. The optical transmittance is slightly reduced, as may be seen by comparing the computer plots in Fig. 1.

2.3 Reflector at $\lambda_0 = 9.4 \mu\text{m}$

The second type of dichroic reflects strongly at $9.4 \mu\text{m}$ and transmits at $16 \mu\text{m}$. It was designed in a similar manner to the dichroic previously described. The same basic period of $\frac{L}{2} \ H \ \frac{L}{2}$ was used, but since substantial reflectance in the $10 \mu\text{m}$ region is desired, the L and H are quarterwaves at $10 \mu\text{m}$, rather than $16 \mu\text{m}$. The equivalent index of the basic period at $16 \mu\text{m}$ is 2.16. In this case the reflector stack has an equivalent index close to that of ZnSe ($n = 2.42$) so no matching layer is needed between stack and substrate. However, the stack must be matched to air at $16 \mu\text{m}$ or unacceptable reflection losses will occur. Thus a single PbF_2 matching layer is placed on top of the stack, with a quarterwave optical thickness at $16 \mu\text{m}$. Since the design is

$$\text{ZnSe} / \left(\frac{L}{2} \ H \ \frac{L}{2} \right)^m \ L' / \text{air}$$

FIG 1

the stack-air layer coalesces with the top PbF_2 layer to form a thick PbF_2 layer. The design is thus:

$$\text{ZnSe}/\frac{L}{2} (H L)^{m-1} L''/\text{air}$$

$$\text{where } L = \text{QWOT} @ \lambda_0 = 9.4 \text{ } \mu\text{m}.$$

$$H = \text{QWOT} @ \lambda_0 = 9.4 \text{ } \mu\text{m}.$$

$$L'' = \frac{L}{2} + L' = \text{QWOT} @ \lambda_0 = 25.4 \text{ } \mu\text{m}.$$

The thicknesses in the design actually coated were adjusted to achieve stress compensation. The net result was to increase the thicknesses of the $\underline{L}$ PbF_2 layers by 15% and to decrease the ZnSe layers by the same amount.

Thus the design that was finally coated is

$$\text{ZnSe}/ 0.58L (.85 H 1.15L)^{m-1} 0.85 H 1.15L''$$

where L , H & L'' are defined in a foregoing paragraph.

2.4 11.3 μm Reflector

Another design was a $\lambda = 11.3 \text{ } \mu\text{m}$ mirror requiring 95% reflectance, on a ZnSe substrate. With a reflectance this high, the substrate material is relatively unimportant. The significant parameters are the ratio of high

to low index in the stack and the absorption. It was found that a 15 layer dichroic design of the type described above had high (~16%) absorption that made the reflectance requirement impossible to meet. Therefore higher index materials were used to reduce the number of layers and also the absorption. Germanium was used as a high index material and lead fluoride as the low index. An ordinary quarterwave stack with two periods was used. Assuming bulk index of 4.0 for germanium and that no absorption is present, the reflection is calculated to be 95%. It is important that PbF_2 layer be contiguous to the substrate when an even number of layers are used. Since the thin film index for germanium is slightly higher than the bulk it was hoped the 95% reflectance could be achieved. The design is simply:

ZnSe L H L H air

3 Experimental procedures

3.1 Objectives

The experimental program included two objectives:

- (a) Determination of the refractive indices of the coating materials; and,
- (b) Deposition of the multilayers.

The refractive index data are useful in modelling the spectral transmittance and reflectance on the digital computer.

3.2 Dispersion data for ZnSe

It is well known that the refractive index of evaporated thin film coating materials seldom is the same as the bulk. But the bulk dispersion data are still useful as a first approximation.

ZnSe has been fabricated as an IR material and its dispersion has been measured quite accurately in bulk form by the National Bureau of Standards.² The thin film indices have been measured by various groups. The data used in modeling the stacks was calculated from a dispersion polynomial determined experimentally on ZnSe deposited by a chemical vapor deposition. The polynomial is of form:

$$n(\lambda)^2 = 1 + \sum_{j=1}^3 \frac{A_j \lambda^2}{\lambda^2 - \lambda_j^2} \quad (2)$$

where the constants are

j	λ_j	A_j
1	0.188077	4.246649
2	0.376652	.6852059
3	49.6950	3.311467

This model uses two UV oscillators and one IR oscillator and is valid over the range of 0.54 to 18.2 μm . Table 1 shows a printout of the indices calculated from Eq. (1).

It also compares the published index data for evaporated ZnSe and bulk material. At worse the bulk index is 2% lower than the film.

3.3 Dispersion data for PbF_2

The PbF_2 index at IR wavelengths was not found in the literature; it was measured. A quarterwave at 16 μm of PbF_2 was coated onto a CdTe substrate. A Perkin Elmer Model 467 IR spectrometer was used to measure its transmittance as a function of wavelength over the region from 2.5 μm to 25 μm . The resulting curve has extrema corresponding to the $\lambda/4$, $\lambda/2$, $3\lambda/4$, etc. points. A quadratic least squares computer program was used to locate the extrema more precisely. Then the resulting wavelength were used to compute indices from the equation:

$$n(\sigma_j) = \frac{j}{\sigma_j} \left[\frac{\sigma_m n(\sigma_m)}{m} \right] \quad (3)$$

where: $\left. \begin{array}{l} \sigma_m = m\sigma_o \\ \sigma_j = j\sigma_o \end{array} \right\} \sigma_o = \text{wavenumber of quarterwave point}$

T A B L E 1

WAVENUMBER IN RECIPROCAL CENTIMETERS	Bulk INDEX	Film index
400	2.247	
440	2.249	
460	2.269	
480	2.266	
500	2.300	
520	2.313	
540	2.323	
560	2.333	
580	2.341	
600	2.346	
620	2.354	
660	2.365	
720	2.377	
780	2.387	
840	2.394	
960	2.405	2.447
1100	2.412	
1340	2.420	
2020	2.430	
2620	2.435	
3000	2.437	
20000	2.438	

The bulk index of ZnSe^2 and also the index of an evaporated film at 940 reciprocal centimeters from the data of Peninoff³ et al.

It is assumed the index is known at some wavenumber λ_n , which is the location of a $(m \frac{\lambda}{4})$ wave point. The index of $\sigma_6 = 3485 \text{ cm}^{-1}$ was taken as $n = 1.75$ which is the bulk index in the red part of the visible.⁴ Table II shows the results of the dispersion measurements. Although PbF_2 index data have been published,⁵ these cannot be fit with a smooth curve and were suspect. Fig. 2 plots the index data. No attempt was made to measure thin film absorption.

3.4 Cleaning of substrates

The first step in coating a multilayer dichroic reflector is to clean the substrate. The procedure is summarized below:

1. Clean off organics by gently rubbing with detergent calcium carbonate mixture.
2. Rinse off under tap water.
3. Clean with spectra grade isopropyl alcohol.
4. Blow with dry N_2 .

The final cleaning is done inside of the evaporation chambre. The substrates are glow discharge cleaned for 20 minutes, as described in a subsequent paragraph.

3.5 Coating Procedure

All of the coatings were prepared in a Balzers BA500 chamber using thermal evaporation. CVD zinc selenide

T A B L E I I

Wavenumber in reciprocal centimeters	Refractive index
690	1.47
1220	1.66
1780	1.71
2340	1.74
2900	1.75
3480	1.75

The refractive index versus wavenumber for
an evaporated layer of lead fluoride,
as obtained from spectrophotometric
measurements.

FIG 2

The measured refractive index (solid points) of a lead fluoride, evaporated layer.

chunks obtained from Raytheon were crushed with a mortar to pieces about a millimeter in diameter. Initially a platinum boat was used to evaporate the zinc selenide. It was found that the boat reacted during evaporation as evidenced by scoring of the platinum. A fresh tantalum boat and material was used on each run to avoid using the same material twice. The lead fluoride was evaporated from a platinum boat. The lead fluoride was supplied by CERAC in the form of vacuum fused irregularly shaped pellets 3 or 4 mm in dimension. Fresh lead fluoride was used for each evaporation.

Both materials were monitored optically in reflection using a He-Ne source. CdTe substrates were monitored via reflection from a germanium slab placed next to the substrate.

The sources were placed close to the center of the chamber, as was the substrate holder. The evaporated materials impinged on the substrate at angles in the range of 4 to 8 degrees. The same jigging and source configuration was used from run to run, with the jigging and electrodes being sandblasted between runs.

Just before cold trapping the substrate was glow discharge cleaned. Argon gas was bled into the system to a pressure of 0.05 to .1 Torr and a voltage was applied

through a feed through to an aluminum glow discharge wand at a current of 300 ma. The glow discharge was maintained for 10-20 minutes, after which the chamber was pumped down.

A liquid nitrogen cold trap was used during all evaporations. The typical run was started by pumping down over night and cold trapping which resulted in a pressure range of 1.0 to 3.0×10^{-6} torr. The lead fluoride was coated at a rate of about one quarterwave/min @ $\lambda_0 = 633$ nm, which corresponds to a physical thickness rate of about 100 nm/min. The pressure was found to increase quite little during PbF_2 evaporation. PbF_2 sublimes and requires continuous adjustment of the electrical power to the boat in order to hold the rate steady.

ZnSe evaporation caused a significant increase in chamber pressure during evaporation, typically 2 or 3 10^{-5} torr. The ZnSe was evaporated at a rate of about 65 nm/min.

The chamber temperature was monitored during evaporation using a copper-constant thermocouple. Chamber temperature always increased significantly while coating ZnSe. When the temperature rose into the range 100°C to 150°C , the chamber was allowed to cool down for several hours since high substrate temperature can cause coatings to peel via mechanical stress. Typically the chamber must be cooled down 2 or 3 times during a 9 layer coating. Such a run takes about 4.5 hours of coating time and 5-8 hours of cooling time.

When the first layer of a coating was PbF_2 , a thin adhesor layer of ZnSe was flashed onto the substrate. Such a layer is about 50-60 nm thick and helps prevent peeling of the coating.

After finishing a multilayer stack, the chamber was allowed to cool down a few hours. Then the chamber was opened, the substrate turned over and a single layer ARC lay of PbF_2 coated on the backside of the substrate.

4. Results

4.1 Reflectance and transmittance

The dichroic mirrors had a peak transmittance of 90% or better, with the exception of some 15 layer coatings. Figure 3 shows that a quite substantial transmittance was attained in the 10 μm region.

Figure 4 shows the transmittance of an 11 layer dichroic reflector deposited upon a ZnSe substrate. It is intended to have a high transmittance at 16 μm and high reflectance at 9.3 μm . The maximum transmittance of 95% is at 13.5 μm , which falls short of the desired 16 μm wavelength. The transmittance 80% at 16 μm is adequate, however. Its reflectance, as measured at LASL, is 87% at $\lambda = 9.3 \mu\text{m}$. The damage testing at LASL showed that it withstood 5 J/cm² at 9.3 μm from a pulsed CO₂ laser.

It was hoped that the addition of more layers -- to 14 layers-- would increase the reflectance. The peak reflectance of the 14 layer coating did not exceed that of the 11 layer design. Figure 5 shows the spectral reflectance of a 14 layer mirror, as measured at LASL. Peak a is the first order interference

Fig.3

Fig.4

FIG 5

and b is the second-order peak. Its spectral transmittance is similar to that of the eleven layer coating (shown in Fig. 4) -- which is indicative of absorption.

4.2 Absorption

Although some of the eleven-layer coatings withstood 5 J/cm^2 fluence levels in the laser, the 15 layer coating cited above had an undesirable amount of absorption. Although its reflectance of 87% might be adequate for many purposes, its absorption precludes its use as an output mirror. It is tempting to attribute the absorption to poor stoichiometry in either the PbF_2 or the ZnSe . Initial Auger electron spectra at LASL (on another sample) showed that the coatings were Se rich by about 2% -- that is the proportion of Zn:Se is 49:51 rather than 50:50.

A correlation of the Auger spectrum with the absorption at $10 \text{ } \mu\text{m}$ could well be the subject of another investigation.

5. References to the literature

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6. Captions to the Figures

1. The computed spectral transmittance of a dichroic mirror of the design

air 0.5 L (H L)⁴ H 1.6 L substrate

for the solid curve. The stress compensated design (dashed) is

air 0.58 L (0.85 H 1.15L)⁴ .85H 1.6L substrate

where the substrate is polycrystalline CdTe, and L and H represent layers of optical thickness

$\lambda_0/4$ at $\lambda_0 = 16 \text{ } \mu\text{m}$ of PbF_2 and ZnSe , respectively. The bulk absorption in the substrate, as well as the Fresnel reflection loss at its nonobverse side, are not accounted for in the calculation.

2. Captioned on drawing.
3. The measured spectral transmittance of a dichroic reflector cited as the stress compensated design in the caption to Fig. 1. The nonobverse side of the substrate is coated with a antireflecting single layer

whose optical thickness is a quarterwave at

$$\lambda_0 = 16 \text{ } \mu\text{m.}$$

4. The measured spectral transmittance of a stress-compensated dichroic mirror of the design

$$\text{air } 2.7L \text{ H } (1.15L \text{ } 0.85H)^4 \text{ } 0.58L \text{ substrate}$$

where the substrate is multicrystalline ZnSe and L and H represent evaporated layers of quarterwave optical thickness at $\lambda_0 = 9.4 \text{ } \mu\text{m}$ of lead fluoride and zinc selenide, respectively.

5. Measured spectral reflectance of a 14 layer stack that reflects $\lambda_0 = 11.3 \text{ } \mu\text{m}$. The design is

$$\text{air } (H \text{ L})^6 \text{ H } 0.5L \text{ substrate}$$

where the substrate is ZnSe and H, L represent layers of optical thickness $\lambda_0 / 4$ of ZnSe and PbF_2 , respectively.