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THIN FILM MATERIALS AND DEPOSITION TECHNIQUES FOR INFRA-RED COATINGS

Richard A. McKyton, et al

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This report describes the coating materials and deposition techniques used for producing film systems in the mid-IR spectral region (2.0 - 14.0 μm). It discusses the selection of coating materials and establishes the optical and physical properties of a low middle and high index film material suitable for film systems designed for use at 10.6 μm. Four IR coating designs were fabricated and their spectral characteristics compared to a computer generated tolerance analysis of the theoretical designs.

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INTRODUCTION

The objective of this study is the establishment of thin film materials and deposition techniques for film system to be used in the mid-IR spectral region (2.0 to 14.0μm). Many materials used in visible applications (.4 to .7μm) cannot be applied to this IR region due to their high absorption and poor durability. Therefore new techniques and coating materials must be evaluated to insure that the IR films have low absorptivity and reasonable durability characteristics. The investigations performed to meet this need include: the selection of materials, determination of optimal deposition parameters, the theoretical design and fabrication of some basic IR film systems and the tolerance analysis of the selected designs.

SELECTION OF COATING MATERIALS

Material Choices

In addition to low absorption and film durability, the materials selected should give a spread of refractive index values which will provide the design flexibility needed for multilayer film systems. From theoretical IR design considerations the following index ranges would be acceptable: low (1.3 to 1.5) middle (2.0 to 2.4) and high (3. to 4.).

From an evaluation of present IR materials it was possible to arrive at materials which meet the IR film designer's criteria. Materials which are toxic or present a radiation hazard e.g., ThF_4 were avoided because of the special handling required. Zinc sulfide ($n = 2.19$ @ 10.0μm) and germanium ($n = 4.00$ @ 10μm) appear to be good middle and high index materials. Both materials are transmitting within the mid-IR region.

Selection of a low index material which would be suitable was difficult because those with the best optical and physical properties are among the toxic materials. For this work the following low index materials and mixtures were investigated to determine which would be the optimal choice:

1 - Calcium fluoride $n = 1.3$ @ 10.0μm

2 - Magnesium fluoride $n = 1.23$ @ 9.0μm

3 - Mixtures of CaF_2, M_gF_2

4 - Mixtures of CaF_2, Al_2O_3 ($n \approx 1.7$)

5 - Glass, SiO_2, ($n = 1.51$)

6 - Cryolite, Na_3AlF_6 ($n = 1.3$)

7 - 1, 2, 3, 6 with protective overcoats

Deposition Techniques and Film Properties

General:

All deposits were made using a fully charged 270° electron beam gun source. Initial work with radiant filament sources proved them to be time consuming (very slow deposition rates) and inefficient (high filament currents and resultant high pressures during deposition). Clean optical grade germanium blanks 1 in. diameter X 1/8 in. thick manufactured by Coherent Radiation were used as substrates except for the germanium films where arsenic trisulfide was used as the substrate material. Conventional glass cleaning techniques - washing with biodegradable soap, tap water rinsing and vapor degreasing in isopropyl alcohol bath were found to give an acceptable germanium surface. Substrates were heated to temperature under vacuum and allowed to soak for one hour prior to deposition. Vacuum was maintained below 5×10^{-5} Torr during deposition by means of a Haas type (side pumped) mechanical/diffusion pump vacuum station equipped with a liquid nitrogen cold trap.

Film thickness was controlled during deposition by a reflectance mode optical thickness monitor. The reflectance from a growing film's surface will be a maximum or minimum whenever the optical thickness of the film reaches an integral number of quarter-waves of the incident light;

Max/Min Reflectivity when:

$$O.T. = nt = m\ \lambda/4,\ m = \text{integer}$$

where n = index of refraction

t = physical thickness

λ = incident wavelength of light

The quarter-wave point is defined when $m = 1$ as $\lambda_o = 4nt$. Since most optical thickness monitors are limited to the visible spectrum it is impossible to monitor quarter-wave films for the mid-IR region directly. However, one can select wavelengths within the range of the monitor such that λ monitor $= \lambda_o/m$. For example a quarter-wave film at 10.0µm could be monitored as sixteen quarters or four full waves at .625µm.

After deposition of each material to a quarter-wave optical thickness at approximately 10.0µm each sample's spectral transmission was measured and its index of refraction determined at the quarter-wave optical thickness wavelength using the following formulae:

$$n_f = \left(-n_s \frac{(R_1^{1/2} + 1)}{(R_1^{1/2} - 1)} \right)^{1/2} \quad \text{for } n_f > \sqrt{n_s}$$

$$= \left(n_s \frac{1 - R^{1/2}}{1 + R_1^{1/2}} \right)^{1/2} \quad \text{for } n_f < \sqrt{n_s}$$

and $R_1 = (1 - T - R_2)/\ (1 - R_2\ (T + 1)\ )$

where n_f = film index

n_s = substrate index

R_1 = reflectance from film/substrate boundary

R_2 = reflectance from substrate/medium boundary

T = measured transmission

The following basic durability tests were performed on each film.

Adhesion: Press scotch tape firmly across film surface, lift tape with quick snap (MIL-M-13508).

Abrasion A: Fifty (50) strokes with ¼ in. thick clean cheese cloth pad across film surface with a 1 lb. force (MIL-M-13508).

Abrasion B: Twenty (20) strokes with abrasion test eraser across film surface with a force of 2 to 2.5 lbs. (MIL-C-675).

Middle Index Material - Zinc Sulfide:

Zinc sulfide, Irtran II, n = 2.2 @ 10µm, manufactured by Kodak was deposited onto germanium substrates heated to temperatures between 300 - 450°F. Figures 1 to 4 show the ZnS film surface, under a 400X microscope, when deposited at 300, 350, 400, 450°F. These figures show the epitaxial growth tendency of ZnS films as the substrate temperature increases. Only films deposited at 350°F showed resistance to the adhesion and abrasion tests as well as to a 24 hr. humidity test at 120°F, 100 percent R.H. Visual inspection of the films showed a definite variation in reflected color, i.e., thickness variation due to the temperature dependent sticking coefficient of ZnS. However, spectral transmission measurements between 2.5 - 25µm did not show any significant variation across the sample. The average quarter-wave point for four ZnS quarter-wave films was 10.25µm or within 3 percent of the desired quarter-wave point at 10.0µm. Calculation of the film's index of refraction gave n = 2.25 @ 10.0µm or the same as the bulk material.

High Index Material - Germanium

Polycrystalline germanium (n = 4.00 @ 10.0µ) was deposited onto arsenic trisulfide substrates (n = 2.4) manufactured by Servo Corporation. Substrate temperatures were varied from ambient to 450°F but temperatures above 400°F were found to cause sagging of the substrate material thus making heating above 400°F impractical. Since germanium is absorbing below 1.8µm it was necessary to use a timed evaporation technique at a fixed source to substrate distance and constant e-gun settings in order to achieve the desired film thickness. The films deposited had no temperature dependence as all were resistant to the durability tests outlined. The thickness variation between five runs of germanium on As_2S_3 were within 10 percent of the desired thickness. The index of refraction was calculated for this high index material to be 4.02.

Low Index Materials

Calcium Fluoride, Irtran III, n = 1.3 manufactured by Kodak was deposited onto germanium at temperatures between 300 - 450°F. All the resultant films showed a very diffuse surface which could not withstand prolonged exposure to the atmosphere without breakdown of its surface. The films were extremely soft and exhibited a definite epitaxial growth at higher substrate temperatures as seen in Figure 5, a 30,000X electron micrograph. The index of refraction was determined to be 1.25 @ 10.0µm based on the average of six runs whose quarter-wave points averaged at 9.968µm. Since none of the films could pass

Figure 1. Surface Structure of λ/4 ZnS Film on Germanium at 300 °F

Figure 2. Surface Structure of λ/4 ZnS Film on Germanium at 350 °F

Figure 3. Surface Structure of λ/4 ZnS Film on Germanium at 400 °F

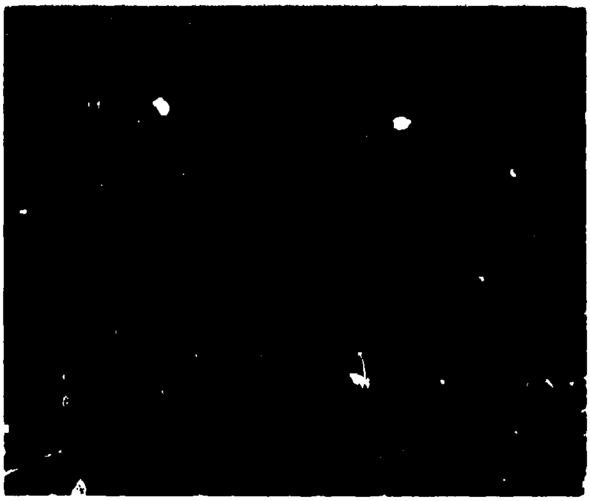

Figure 4. Surface Structure of λ/4 ZnS Film on Germanium at 450 °F

the adherence or abrasion tests another film was deposited onto Ge heated to 540°F (280°C). This provided only slight improvement in the resultant film's physical properties.

Figure 5. CaF_2 Film on Ge

__Magnesium Fluoride__, Irtran I, n = 1.23 @ 9.0μm manufactured by Kodak is already established as a durable low index material for use in the visible spectrum when deposited onto heated substrates (350°F). There is, however, a high stress condition present in these films when deposited to an excessive thickness. A quarter-wave film at 6.0μm was deposited onto bare germanium and over a quarter-wave ZnS film on germanium. From previous work, had the MgF_2 film been deposited to a QWOT at 10.0μm there would be no doubt of film breakdown. The MgF_2/ZnS system allows the MgF_2 film to be deposited on a film of opposite stress which often reduces the film breakdown and which is a desirable film combination from a design standpoint. Unfortunately neither the MgF_2 on germanium nor the low-high index combination was successful as each film had complete mechanical failure when exposed to the atmosphere.

Calcium Fluoride/Magnesium Fluoride Mixtures - Alloys of CaF_2/MgF_2 result in a range of low index valued films which might possess improved physical properties for middle-IR work. Controlled mixtures of 4 to 10 parts CaF_2 to MgF_2 were prepared and quarter-wave films using each mixture were deposited onto germanium at 280°C. Table I gives the physical properties of these mixtures as quarter-wave films at 6.0μm All of these alloys minimized the epitaxial growth of straight CaF_2. The greater the MgF_2 to CaF_2 ratio the more acceptable are the physical properties. The 4/1 ratio mixture offers the best durability but suffers from the mechanical stress of thick MgF_2 films when breathed upon.

Calcium Fluoride/Aluminum Oxide Mixtures - A substitution of Al_2O_3. ($n = 1.7$) for MgF_2 in combination with CaF_2 proved unsuccessful. The melting temperature difference between the two compounds prevented successful co-evaporation.

Schott e-gun Glass - A form of quartz ($n = 1.47$ @ N_D) specially prepared for electron beam evaporation was deposited onto germanium at 280°C. The resultant quarter-wave film was extremely durable but highly absorbing (∿20%) in the mid-IR region.

Protective Coatings on Low Index Film Materials - Various combinations of low index materials were evaluated to determine if any further improvement in the physical properties could be achieved. All of the films were deposited to a quarter-wave optical thickness at 6.0μm. Table II lists the combinations tested along with their principal shortcomings. Cryolite, a very soft and hydroscopic material, when overcoated with MgF_2 was found to offer the best film properties. This film was clear and did not break down upon exposure to atmosphere. Wiping with isopropyl alcohol soaked tissue did not affect the film nor did the adherence nor two abrasion tests. Only after 20 strokes of the abrasion test eraser did the film surface show fine scratches. Forty strokes of the eraser did not appear to further damage the film. There was, however, some slight absorption (∿½%) attributed to the MgF_2 overcoat.

IR COATING DESIGNS

General

Four basic IR film designs were theoretically generated which would decrease the reflection losses on germanium windows and lenses used in the mid-IR spectrum. These four designs were fabricated from the three coating materials chosen: Cryolite with MgF_2 overcoat ($n \sim 1.3$), zinc sulfide ($n = 2.2$), and germanium ($n = 4.0$). The

TABLE I

Properties of CaF_2/MgF_2 Mixtures

Mixture Ratio	4/1	5/1	6/1	7/1	10/1
Substrate temp.	280°C	280°C	280°C	280°C	280°C
film clarity	no cloudiness or diffuse R	clear	very slight haze to film surface	clear	slight haze
Exposure to atm.	no breakdown	*	no effect	no effect	no effect
Alcohol wipe	no effect	*	scratches & removes film	scratches	scratches
Adherence	no effect	*	50% removed	no effect	no effect
Abrasion A	no effect	*	**	removes some of film	fine scratches
Abrasion B	fine scratches	*	*	severe scratches	severe scratches
Breath Condensation	film crazes completely	film crazes	no effect	no effect	momentary cloud effect disappears after few minutes

* Not tested, film crazed under breath condensation

** Not tested, 50% of film removed by adherence test

Adhesion: Press scotch tape firmly across film surface, lift tape with quick snap (MIL-M-13508).

Abrasion A: 50 strokes with ½" thick clean cheese cloth pad across surface with force of at least 1.0 lb. (MIL-C-13508).

Abrasion B: 20 strokes with eraser (abrasion test quality) across film surface under force of 2 to 2.5 lbs. (MIL-C-675).

TABLE II

Protective Films on Low Index Materials

1. CaF_2 with 1/8th wave MgF_2 overcoat

    Substrate temperature: 280°C

    Diffuse film surface

    Abrasion A - scratches severely

2. 4/1 CaF_2/MgF_2 mixture with 1/8th wave MgF_2 overcoat

    Substrate temperature: 280°C

    Film crazed when exposed to atmosphere

3. 7/1 CaF_2/MgF_2 mixture with 1/4 & 1/8th wave MgF_2 overcoat

    Substrate temperature: 280°C

    No improvement over unprotected film

4. 7/1 CaF_2/MgF_2 mixture with 1/4 & 1/8th wave glass overcoat

    Substrate temperature: 450°F

    Fairly resistant to durability tests

    Highly absorbing in Mid-IR

5. Cryolite with 1/8th & 1/4 wave glass overcoat

    Substrate temperature: ambient

    Film surface durable

    Absorbing in Mid-IR

6. Cryolite with 1/4 wave MgF_2 overcoat

    Substrate temperature 350°F

    Very durable

    Little absorption ($\sim\frac{1}{2}\%$)

four designs are:

1. Single layer AR for use at 10.6μ.

   Ge - M - AIR, M - (n = 2.2), QWOT @ 10.6μm

2. Two layer AR film for use at 6.0μm

   Ge - ML - AIR,M - (n = 2.2), QWOT @ 8.4μm
   L - (n = 1.3), QWOT @ 5.9μm

3. Double-Quarter AR film for use at 6.0μm

   Ge - ML - AIR,M - (n = 2.2),QWOT @ 6.0μm
   L - (n = 1.3),QWOT @ 6.0μm

4. Two Layer IR film for use at 10.6μm

   Ge - LH - AIR,L - (n = 1.3), QWOT @ 3.36μm
   H - (n = 4.0), QWOT @ 2.36μm

Fabrication

Each design was deposited onto clean optical grade germanium blanks heated to 350°F. A fully charged 270° multi-source electron beam gun was used to evaporate the required materials. Vacuum was maintained between 2×10^{-6} - 2×10^{-5} Torr for all depositions. Film thickness for each material, except Ge, was controlled by optically monitoring the increasing film thickness as a function of its reflectance. Deposition times ranged from 4 to 17 minutes. After each film system was deposited, the sample was allowed to cool to ambient in vacuum before exposure to atmosphere. The spectral transmission of each design was measured on an IR-spectrophotometer between 2.5 - 25.0μm. Each sample was then returned to vacuum and the back surface coated with the same film system. The double coated samples were also measured on the IR-spectrophotometer. Figures 6 through 9 and 10 through 13 show the theoretical and experimentally measured transmission spectra for each film design with a single (one surface) and double (both surfaces of substrate) coating on germanium.

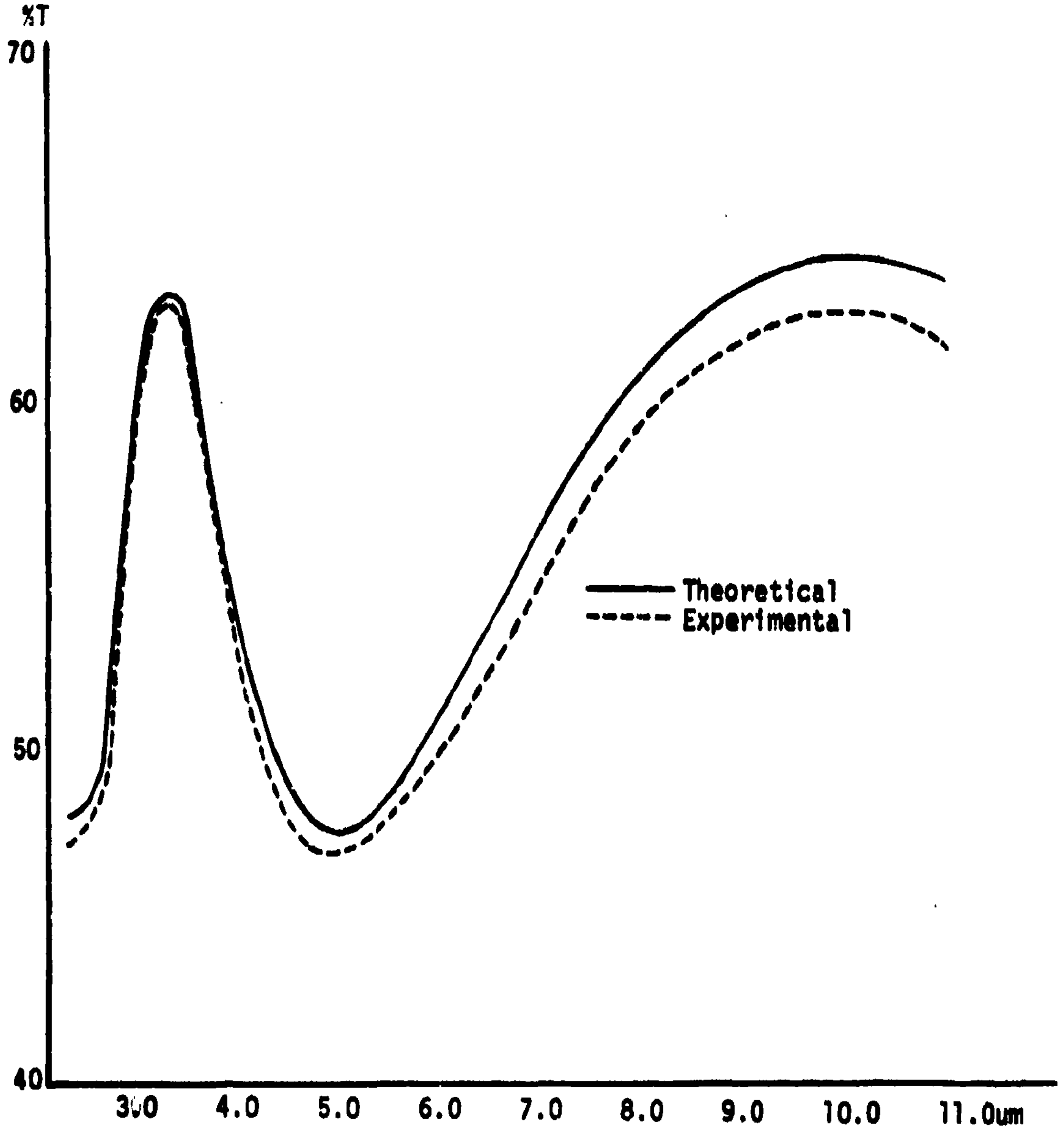

Figure 6. Single Layer A-R Film (Ge-M-Air) on One Surface

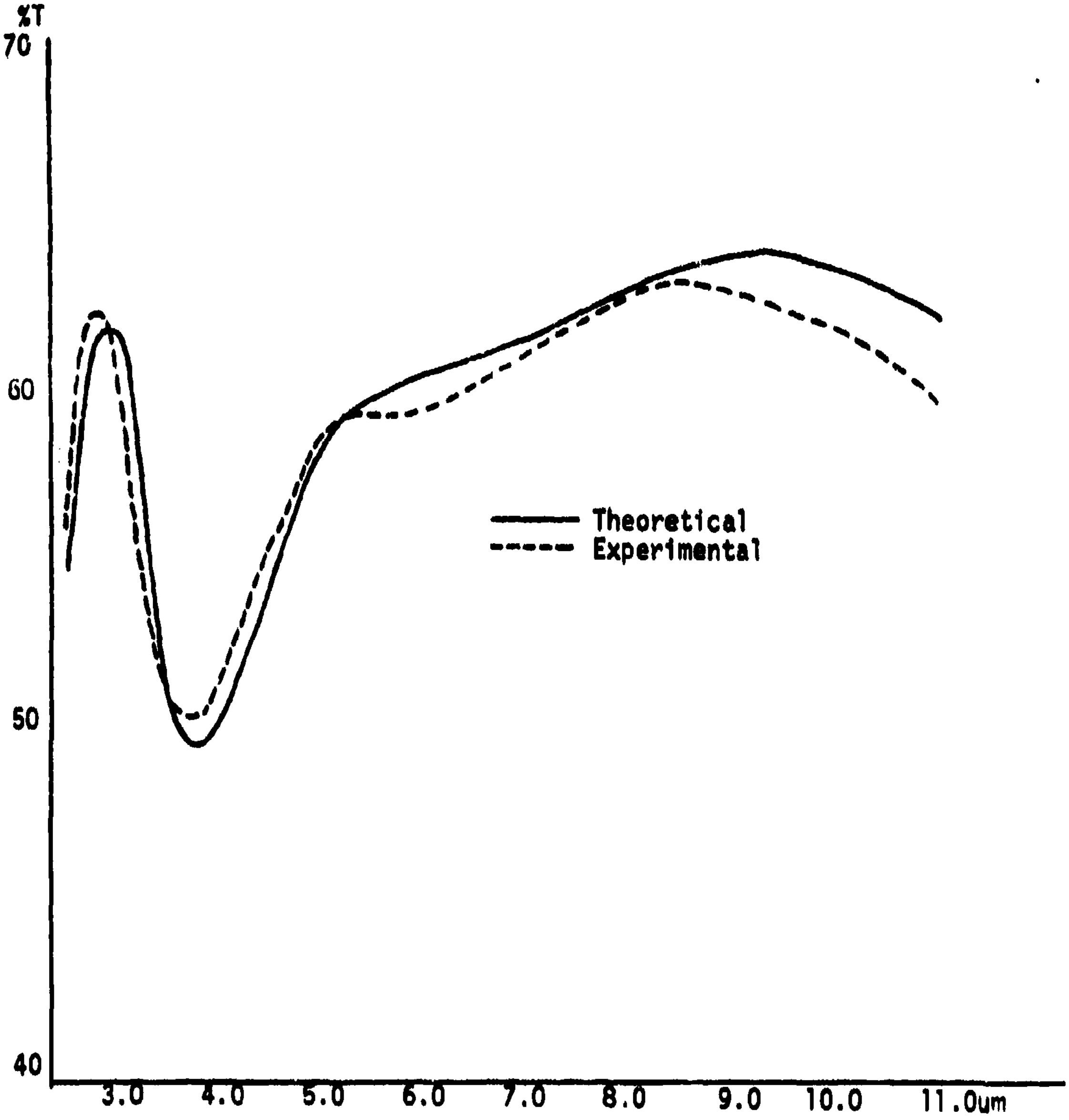

Figure 7. Two Layer AR Film (Ge-ML-Air) on One Surface

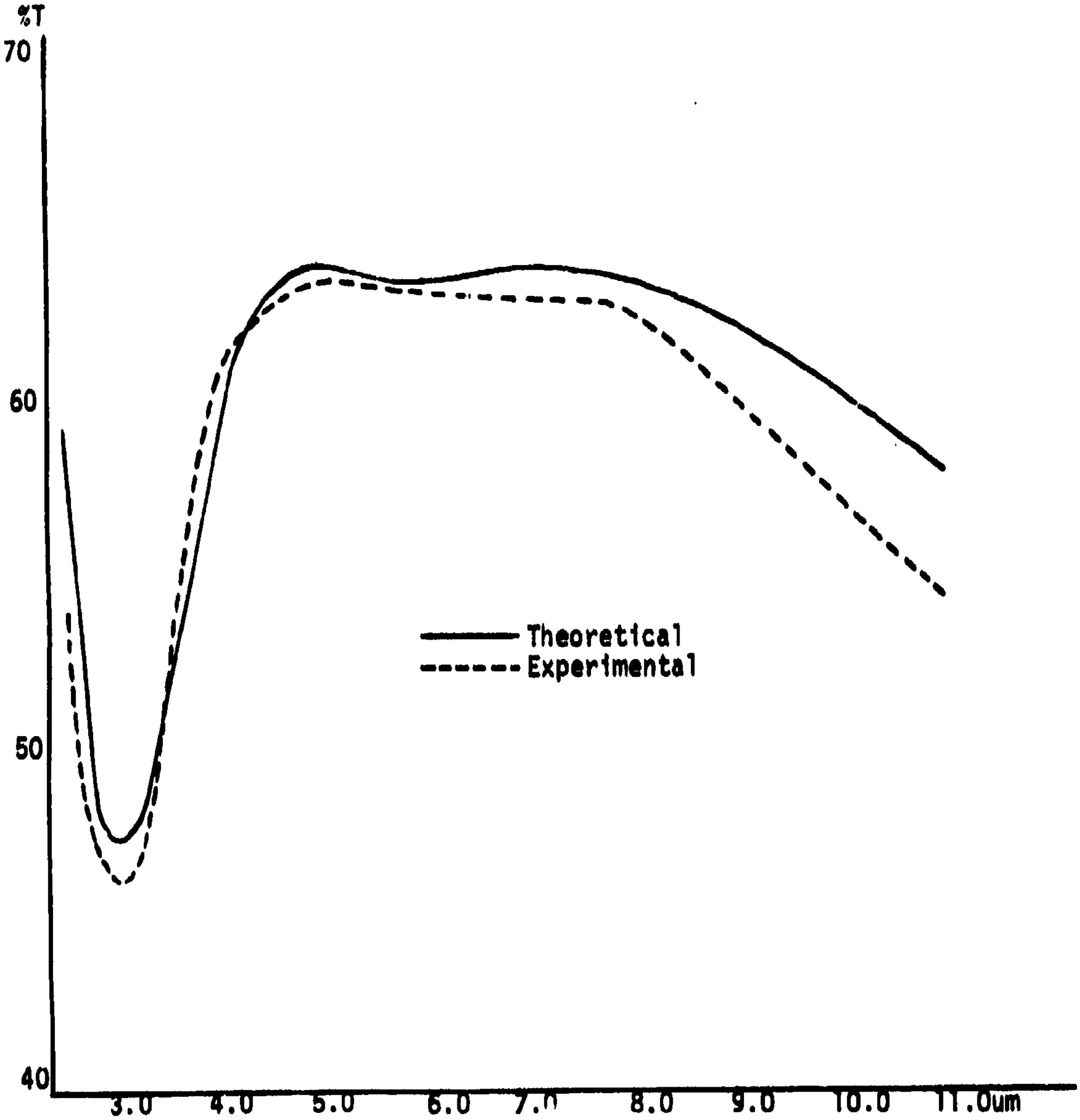

Figure 8. Two Layer AR Film, Double Quarter, (Ge-ML-AIR) on One Surface

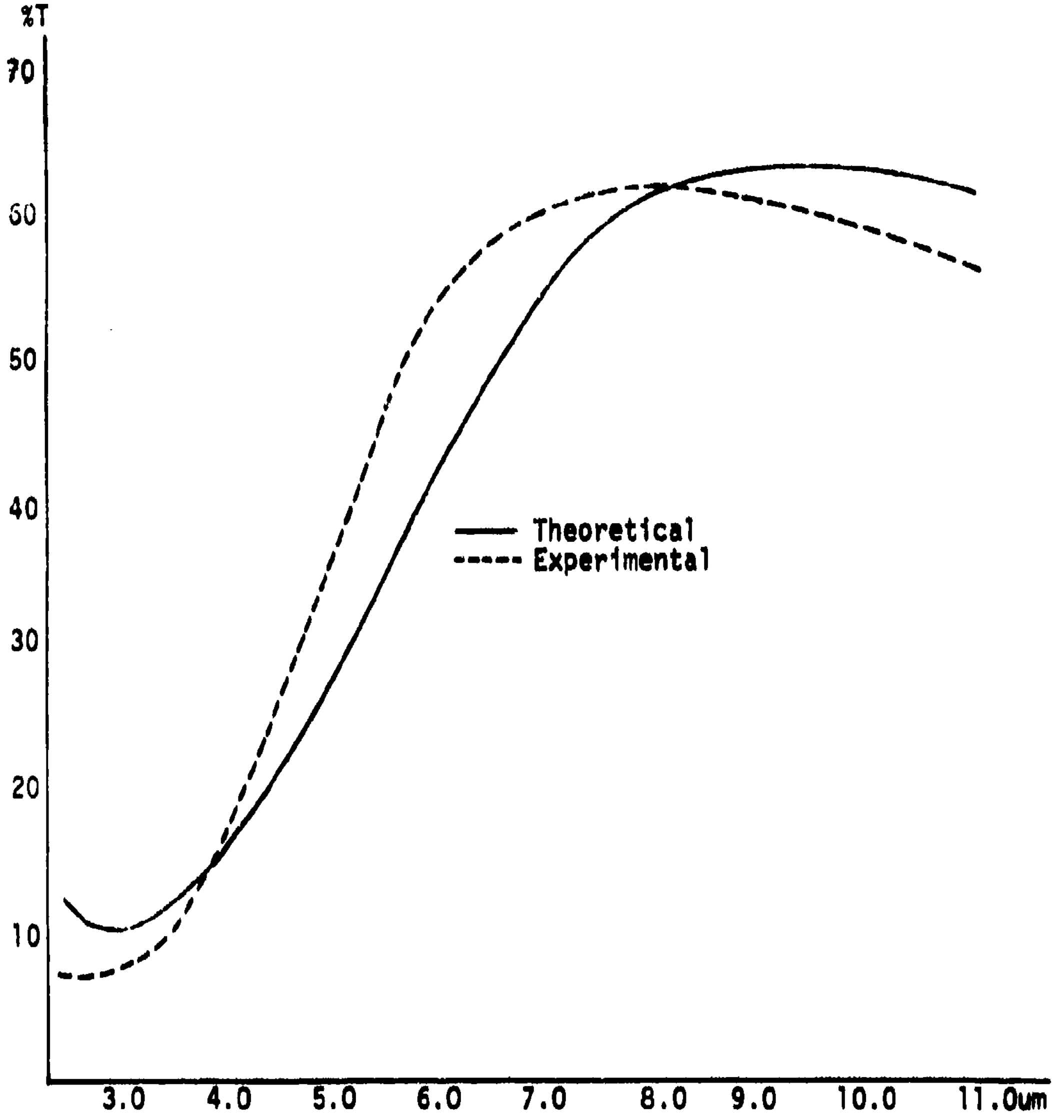

Figure 9. Two Layer AR Film (Ge-LH-Air) on One Surface

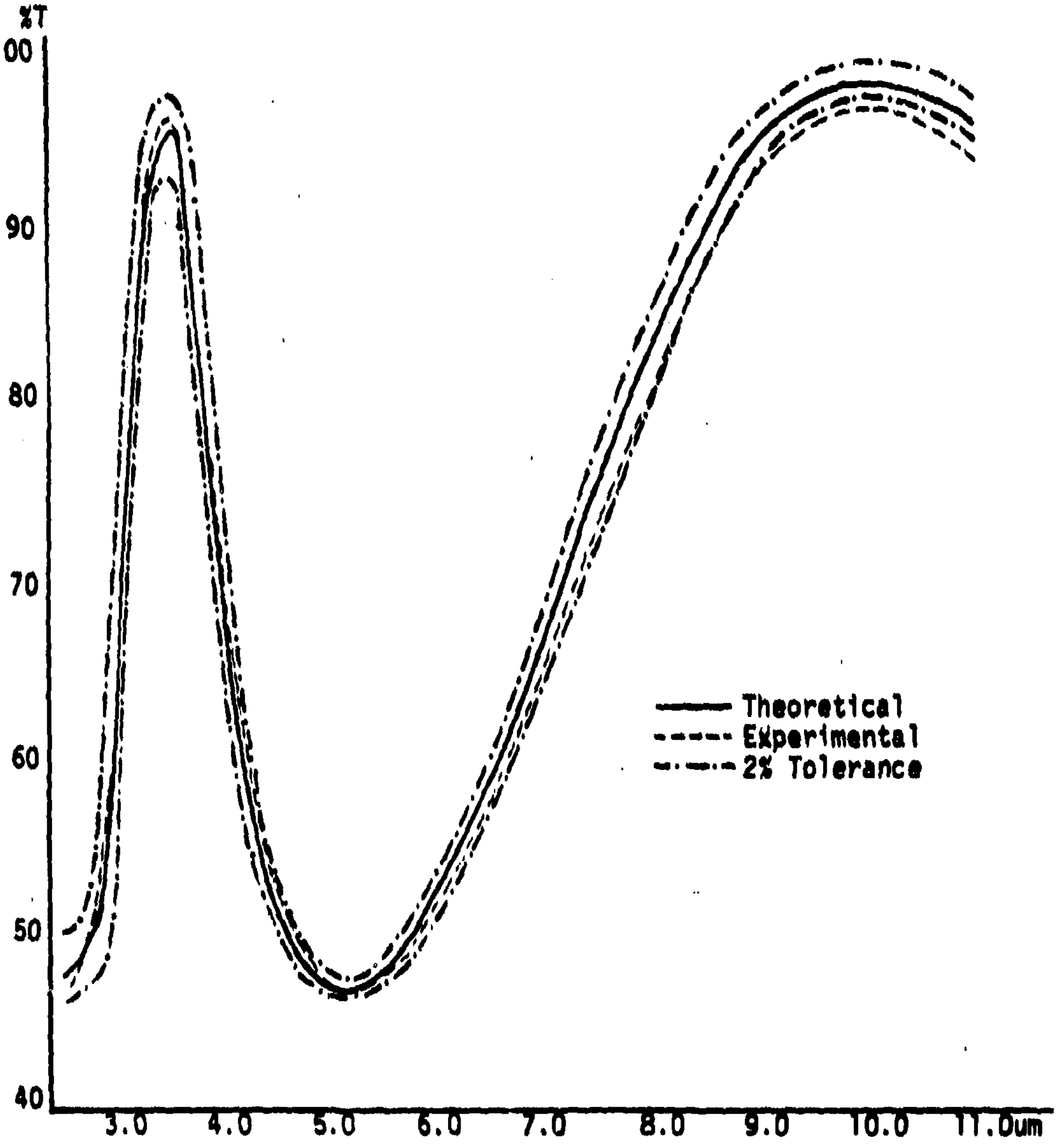

Figure 10. Single Layer AR Film (Ge-M-Air) on Two Surfaces

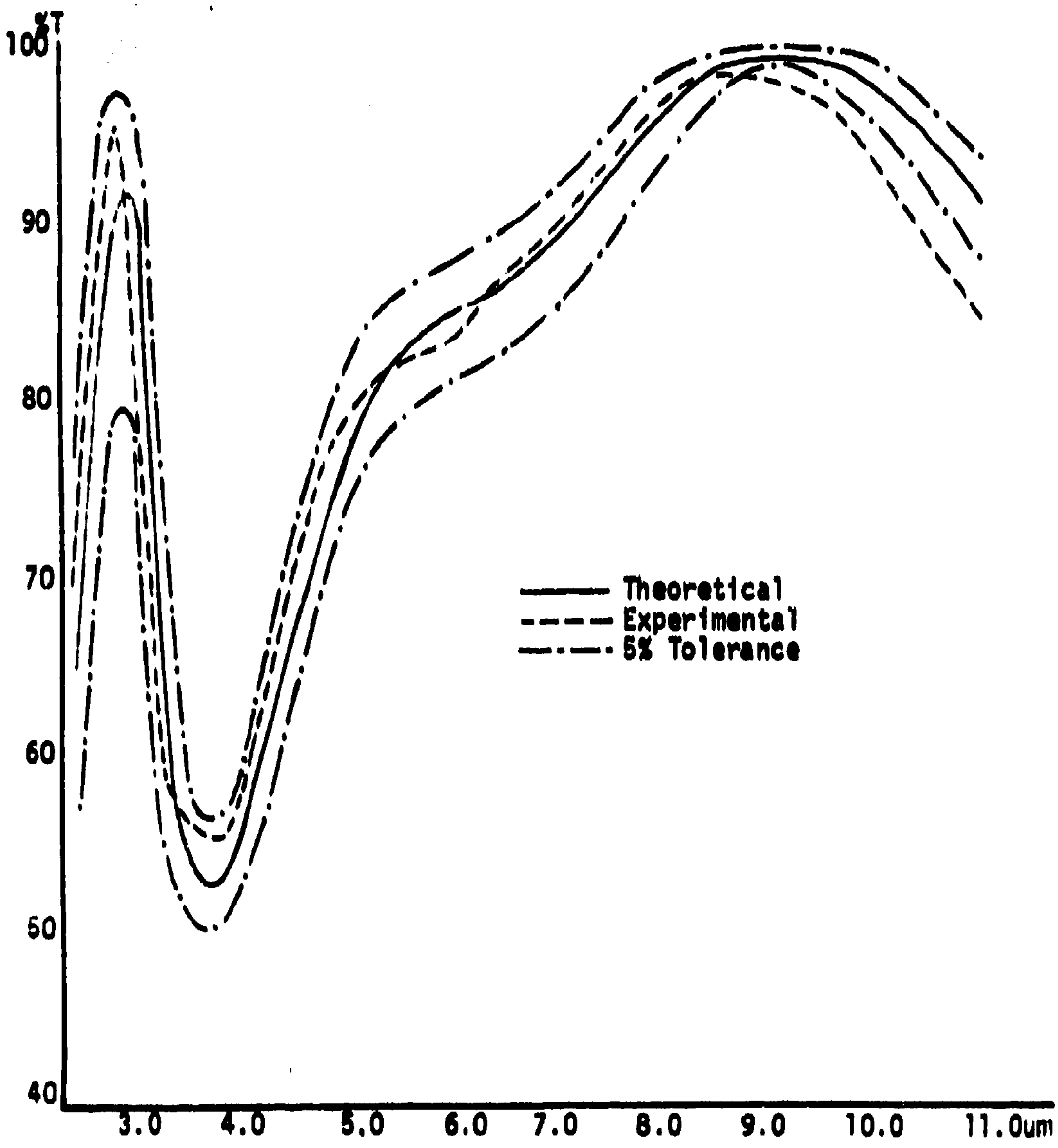

Figure 11. Two Layer AR Film (Ge-ML-Air) on Two Surfaces

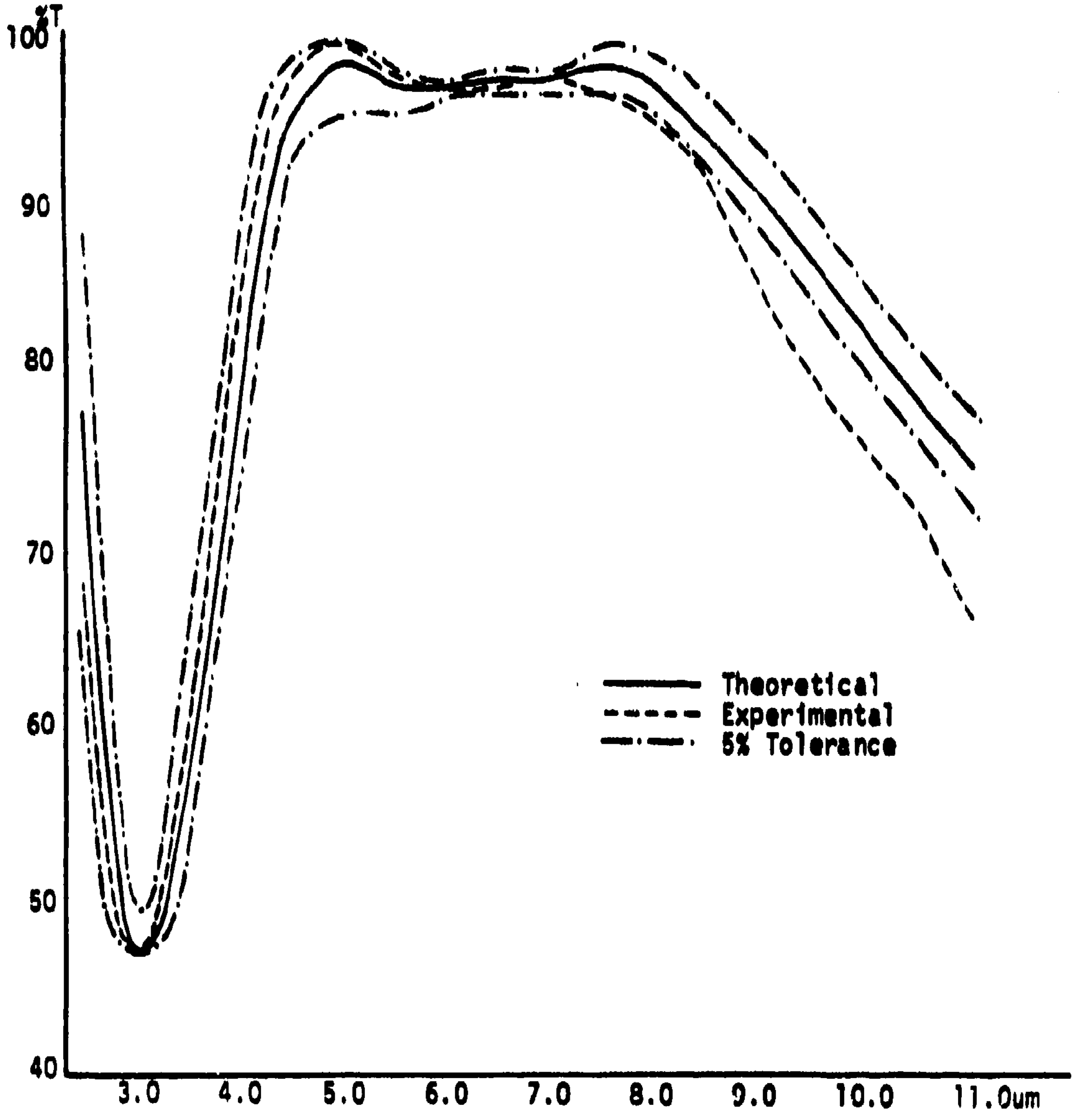

Figure 12. Two Layer AR Film — Double Quarter (Ge-ML-Air) Two Surfaces Coated

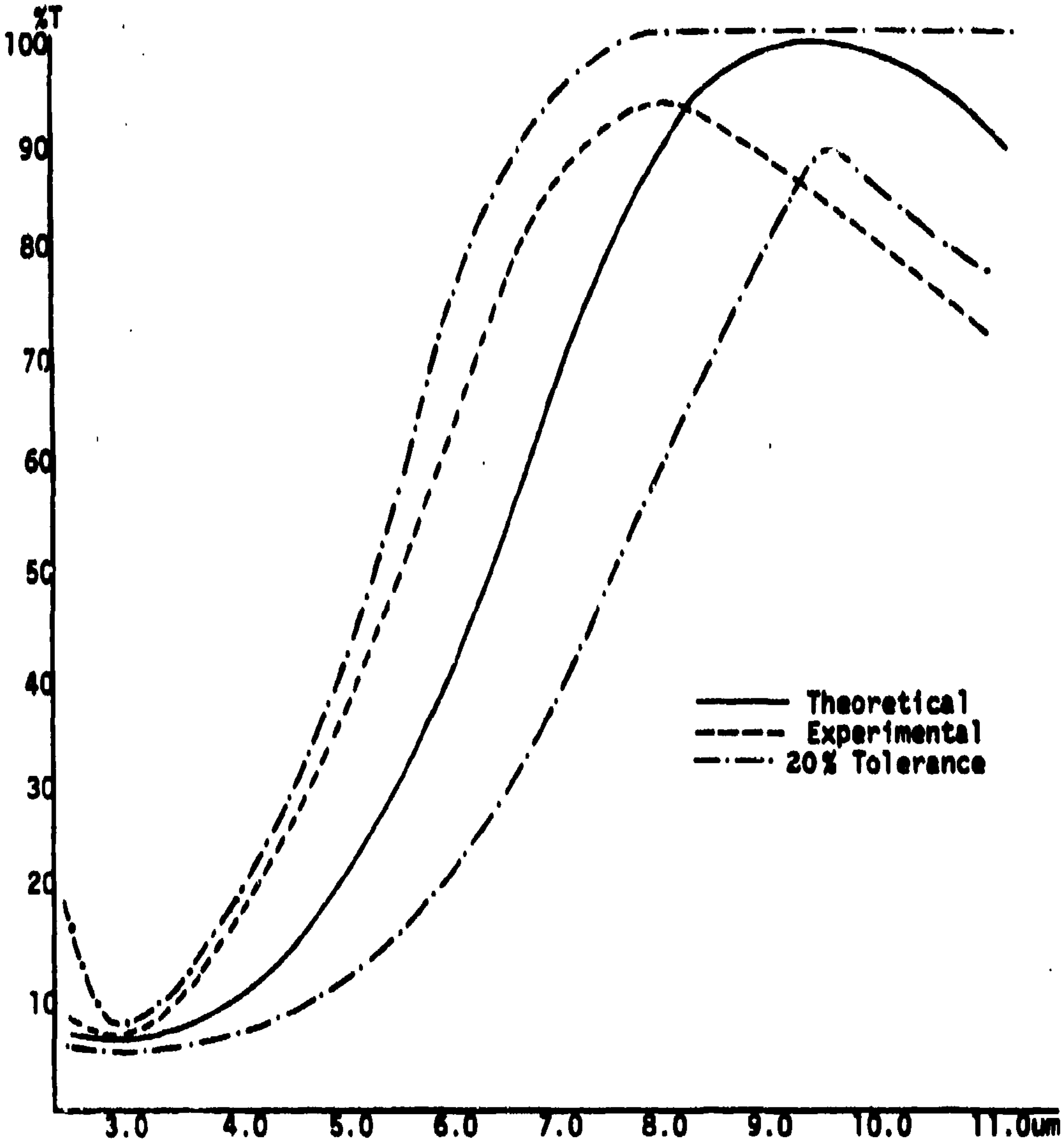

Figure 13. Two Layer AR Film (Ge-LH-Air) on Two Surfaces

Tolerance Analysis

As is evident from both sets of curves for the single and double surface coatings there is some disagreement between the theoretical or ideal spectral performance and the measured transmission. Using an in-house thin-film tolerance analysis program it is possible to analyze the designs to determine what film thickness error spread would cause this difference. Also the program can determine which film's thickness is critical in the resultant multilayer's spectral performance. Shown in Figures 10 to 13 are the transmission tolerance envelopes for each multilayer design applied to both surfaces of a germanium substrate. All of the envelope curves are well fitted to experimental data except beyond 9.0μm where absorption characteristics of the substrate and films are not included.

The tolerance analysis of the single layer AR coating indicates that a 2 percent maximum film thickness error would result in the measured spectral performance. A 5 percent film thickness tolerance would account for the experimental transmission data of the two middle-low index film systems. The last film design, Ge-LH-AIR, would have resulted if a 20 percent thickness tolerance was experienced. This large tolerance difference between the last system and the three other coatings is reasonable since the thickness of high index film, germanium, had to be monitored using a fixed timed deposition technique while the other coatings were monitored directly by the reflectance method. A modified optical thickness monitor for use beyond 1.8μm, incorporating IR-transmitting windows, IR-source and detector, would allow direct monitoring of germanium films with thickness control within the 2 to 5 percent range of the other IR-materials.

An analysis of the individual layer sensitivity of each middle-low index. two layer design, indicated that the middle index film error results in greater changes in the system than the low index film. For the low-high index film each layer's thickness appeared to be equally significant in the resultant spectral performance of the two layer stack.

SUMMARY AND RECOMMENDATIONS

The evaluation of conventional coating materials and their application to middle-IR film systems indicate that it is practical to fabricate single and multilayer films with the desired optical and physical properties.

Middle and high index materials, zinc sulfide and germanium can be readily used in IR film applications. No satisfactory common low index material was found with acceptable optical and physical characteristics. Modified low index materials, alloys or protective overcoatings can be employed if one can work with somewhat reduced physical and optical properties. Magnesium fluoride overcoated on cryolite results in a low index film with improved durability but also having slight absorption.

A technique for depositing IR-film designs with the desired optical thickness has been established. It is possible with a standard reflectance mode optical film monitor to achieve the desired film thickness by monitoring higher ordered quarter-wave points. Typically 2 to 5 percent accuracy is attainable with minimal care.

Because of the importance of films for use in this spectral region 4.0 to 1.40μm and especially 10.6μm other materials despite their toxicity and safety hazard should be considered. Thorium fluoride though radioactive certainly should be used, since it is a hard durable low index material. This laboratory is actively seeking Army licensing for this material and has established the safe operating procedures needed for it and toxic materials such as cadmium telluride, lead telluride, arsenic trisulfide and others.