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PROGRESS IN THE DEVELOPMENT OF A DURABLE SILVER-BASED HIGH-REFLECTANCE COATING FOR ASTRONOMICAL TELESCOPES

The University of Arizona

Ph.D. 1985

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PROGRESS IN THE DEVELOPMENT OF A DURABLE SILVER-BASED
HIGH-REFLECTANCE COATING FOR ASTRONOMICAL TELESCOPES

by
Dar-Yuan Song

A Dissertation Submitted to the Faculty of the
COMMITTEE ON OPTICAL SCIENCES (GRADUATE)
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

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As members of the Final Examination Committee, we certify that we have read
the dissertation prepared by Dar-yuan Song

entitled Progress in the Development of a Durable Silver-based
High-reflectance Coating for Astronomical Telescopes

and recommend that it be accepted as fulfilling the dissertation requirement
for the Degree of Doctor of Philosophy.

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June 17, 1985

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SIGNED: _____

Dan Yuen Song

DEDICATION

To my parent, and my wife.

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TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS	vii
LIST OF TABLES	xii
ABSTRACT	xiii
1. INTRODUCTION	1
Orgnization of the Dissertation	6
2. BASIC THEOREY	10
The Characteristic Matrix of a Thin Film	10
Effect of Angle of Incidence	16
Boosted Reflectance of a Metal	19
Admittance Diagram	21
Overcoats	26
Electric Field Distribution in the Multilayer Coating	28
Surface Plasmons at a Metal Surface	32
Light Coupling to Surface Plasmons	39
3. INITIAL APPROACH	41
Theoretical Design	41
Design 1: Reflectance-boosting Coating	42
Design 2: Silver Overcoat on Aluminum	44
Experimental Results	47
Coating 1: Reflectance-boosting Coating	49
Coating 2: Silver Overcoat on Aluminum	51
4. UNIFORMITY REQUIREMENTS AND TOLERANCES	55
Manufacturing Tolerances	55
Coating Uniformity	60
Monitoring Methods	67
5. ENVIRONMENTAL TESTS	77
Durability of the Candidate Coatings	78
Improved Durability of the Copper-based Coating	83
Surface Plasmon of the Silver-based Coating	87

TABLE OF CONTENTS--Continued

	Page
6. ANALYSIS.....	96
Rate of Corrosion in Sulfur	96
Grain Size Electron Microscopy.....	99
Optical Microscopy of Grain Size after Corrosion.....	102
Copper and Aluminum Overcoats on Silver.....	107
Rutherford Backscattering Results.....	109
Model for the Durability Improvement.....	109
7. FIELD TEST	112
8. CONCLUSION	119
Summary	119
Suggestions for Further Work	122
LIST OF REFERENCES.....	125

LIST OF ILLUSTRATIONS

Figure		Page
1.1.	Comparison of reflectance between aluminum and silver in the ultraviolet and visible region.....	7
1.2.	A photograph of the 1.2 M primary mirror of the infrared telescope showing the progress of the corrosion after 10 months of service	8
2.1.	Schematic drawing of a single layer, with forward and backward travelling waves.....	13
2.2.	Admittance diagram showing the locus of a single layer with refractive index of n.....	24
2.3.	Admittance diagram with isophase contours and isoreflectance contours.....	25
2.4.	Admittance locus of a boosting coating over silver. The design is $\text{Air} \text{Ta}_2\text{O}_5 \text{SiO}_2 \text{Ta}_2\text{O}_5 0.8\text{Al}_2\text{O}_3 \text{Ag}$ at reference wavelength 300 nm.....	27
2.5.	Admittance locus of a boosting coating over silver with the same design as in Fig. 2.4. but reference wavelength at 320 nm.....	29
2.6.	Electric field contours on an admittance diagram.....	31
2.7.	Schematic drawing of the metal-dielectric interface.....	33
3.1.	(a) Calculated reflectances for coating of design : $\text{Air} \text{H L H M Ag} \text{Glass}$ in the visible region.....	45
3.1.	(b) Calculated reflectances for the same coating design as in Fig. 3.1. (a) but in the infrared region	46
3.2.	Calculated reflectances for coating of design : $\text{Air} \text{H M Ag M' Al} \text{Glass}$ in the visible region.....	48
3.3.	Measured reflectances for coating of design : $\text{Air} \text{Sb}_2\text{O}_3 \text{Na}_3\text{AlF}_6 \text{Sb}_2\text{O}_3 \text{Si}_2\text{O}_3 \text{Ag} \text{Glass}$	50
3.4.	Measured reflectances of simple silver overcoated aluminum without protection or boosting layers.....	52

LIST OF ILLUSTRATIONS--Continued

Figure	Page
3.5. Measured reflectances of silver overcoated aluminum with two boosting layers.....	54
4.1. The effect of random thickness errors of 10 % standard deviation on the reflectance boosting coating over silver.....	57
4.2. The effect of random thickness errors of 5 % standard deviation on the reflectance boosting coating over silver.....	58
4.3. The effect of random thickness errors of 10 % standard deviation on the silver overcoated aluminum.....	59
4.4. Diagram showing the origin of the terms in the calculation of the wavefront error resulting from a lack of coating uniformity	62
4.5. Uniformity requirements for the reflectance boosting coating over silver if the wavefront error is not to exceed $+\frac{\lambda}{40}$ or $+\frac{\lambda}{20}$	63
4.6. Uniformity requirements for the reflectance boosting coating over silver if the wavefront error is not to exceed $-\frac{\lambda}{40}$ or $-\frac{\lambda}{20}$	64
4.7. Uniformity requirements for the silver overcoated aluminum if the wavefront error is not to exceed $+\frac{\lambda}{40}$ or $+\frac{\lambda}{20}$	65
4.8. Uniformity requirements for the silver overcoated aluminum if the wavefront error is not to exceed $-\frac{\lambda}{40}$ or $-\frac{\lambda}{20}$	66
4.9. The geometrical setup of the coating plant BA510.....	76
5.1. Sideview of the humidity chamber.....	79
5.2. Photographs of the surfaces of coatings after varying degrees of exposure to 94 % relative humidity at 40 °C. (a) Front and (b) rear surface after 20 hours' exposure of a coating of design : Air Al ₂ O ₃ Ag Glass	80
5.2. (c) Front and (d) rear surfaces after 2 days' exposure of a coating of design (Kp-105-1): Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Glass	81

LIST OF ILLUSTRATIONS--Continued

Figure	Page
5.2. (e) Front and (f) rear surfaces after 2 days' exposure of a coating of design (Kp-105-3): Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Glass	82
5.2. (g) Front and (h) rear surfaces after 7 days' exposure of a copper-based coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Cu Glass	85
5.3. Measured reflectance of coating after five minutes' exposure to the atmosphere above a solution of 2ml 22% (NH ₄) ₂ S in 18 ml water. The silver in each case was 100nm thick and the copper 40nm thick	86
5.4. Measured and calculated performance of the boosted silver coating with copper underlayer	88
5.5. (a) Electrical field distribution inside a coating of design: Air 0.8Al ₂ O ₃ Ag, with reference wavelength 300 nm but calculated at 380 nm	90
5.5. (b) Electrical field distribution inside a coating of design: Air Ta ₂ O ₅ 0.8Al ₂ O ₃ Ag, with reference wavelength 300 nm but calculated at 380 nm	91
5.5. (c) Electrical field distribution inside a coating of design: Air SiO ₂ Ta ₂ O ₅ 0.8Al ₂ O ₃ Ag, with reference wavelength 300nm but calculated at 380nm	92
5.5. (d) Electrical field distribution inside a coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ 0.8Al ₂ O ₃ Ag, with reference wavelength 300nm but calculated at 380nm	93
5.6. Measured performances of the boosted silver coating with copper underlayer. (a) with a single Al ₂ O ₃ layer, (b) with (Ta ₂ O ₅ 0.8Al ₂ O ₃) two layers, (c) with (SiO ₂ Ta ₂ O ₅ 0.8Al ₂ O ₃) three layers, and (d) with (Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ 0.8Al ₂ O ₃) four layers	94
6.1. Measured reflectance of 100nm silver with underlayer of 40nm copper. The points are theoretical figures from Hass and Hadley	97
6.2. Schematic diagram of experimental setup for the rate corrosion measurement	98

LIST OF ILLUSTRATIONS--Continued

Figure	Page
6.3. Reflectance with respect to time for four different film designs exposed to the ammonium sulfide solution described in the text.....	100
6.4. Reflectance with respect to time for the four different films of figure 6.3 with an expanded time scale to show the constant reflectance region for film with the copper underlayer.....	101
6.5. Transmission electron micrographs of shadowed replicas of (a) a 100nm silver film on glass and (b) a 100nm silver film over a 40nm copper film.....	103
6.6. The corroded plain silver coating taken in an optical microscope (a) in reflection mode, (b) in transmission mode. The coatings were exposed to the ammonium sulfide solution described in the text.....	104
6.6. (c) The corroded silver over gold coating taken in an optical microscope in reflection mode, (d) in transmission mode.....	105
6.6. (e) The corroded silver over copper coating taken in an optical microscope in reflection mode, (f) in transmission mode.....	106
6.7. Results of a corrosion test in which a 100nm silver film with copper and aluminum overlayers on opposite edges was subjected to atmospheric exposure above a solution of 2ml 22% $(\text{NH}_4)_2\text{S}$ in 18ml water. (a) shows the appearance of the strip of silver next to the edge of the aluminum and (b) shows that of the silver next to the copper. The strip of uncorroded material in (b) is approximately 0.7 mm wide, or seven times that in (a).....	108
6.8. Rutherford Backscattering data showing the number of backscattered helium nuclei as a function of ion energy, which is proportional to the mass of the scattering nuclei in the film material. The highest atomic mass is that of silver, which appears as the peak on the right. The small concentration of copper on the film surface appears next as a very small peak, followed by the larger peak for the copper underlayer itself. The energies of the latter are reduced by passage of the ions through the overlaying silver layer. Lower mass elements in the substrate appear on the left side of the curve.....	110

LIST OF ILLUSTRATIONS--Continued

Figure	Page
7.1. Picture of the sample holder which was mounted on 4-meter telescope.....	113
7.2. (a) Reflectance for coating of design: Air Al ₂ O ₃ Ag Glass, exposed for one year on Kitt Peak. Solid and dashed lines show reflectance before and after the test	114
7.2. (b) Reflectance for coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Glass, exposed for one year on Kitt Peak. Solid and dashed lines show reflectance before and after the test	115
7.2. (c) Reflectance for coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Cu Glass, exposed for one year on Kitt Peak. Solid and dashed lines show reflectance before and after the test.....	116
7.3. Photograph of film after exposure for one year on Kitt Peak: (a) coating of design: Air Al ₂ O ₃ Ag Glass; (b) coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Glass; (c) coating of design: Air Ta ₂ O ₅ SiO ₂ Ta ₂ O ₅ Al ₂ O ₃ Ag Cu Glass....	118

LIST OF TABLES

Table	Page
1. Measured normal emissivity over the entire spectrum for aluminum, copper, and silver.....	4
2. Calculated normal spectral emissivities at 6 and 10 μm are shown for aluminum, gold, and silver. The optical constants were obtained from Hass and Hadley, American Institute of Physics Handbook; those for gold refer to bulk rather than thin film form.....	5

ABSTRACT

Infrared astronomical observations have been severely limited by the radiation emitted by the aluminum coated surfaces of telescope mirrors. Hence, the reduction of emissivity with retention of coating durability for telescope optics is now an important area of study essential for the improvement of infrared astronomical observations. To avoid the considerable effort that a search for a new material superior to aluminum would demand with uncertain outcome, only existing materials were investigated and silver with a protective dielectric layer was thought to be a possible solution. Experiments at Kitt Peak National Observatory showed that the optical performance of a silver coating is better than aluminum in the infrared and visible regions, but even with a sapphire overcoating the silver proved to have such poor environmental resistance that an experimental mirror had to be recoated after just ten months in service. Thus, the improvement of the durability of a silver-based high reflectance coating becomes a key issue that has to be solved for such a coating to be selected for infrared astronomy. Furthermore, most telescopes are used also in the ultraviolet and so any successful coating would need to reflect well in this region. Silver is poor also in this respect.

In this dissertation, we describe the development of a silver-based high reflectance coating that can withstand the humidity and pollution common in the open air and which has good ultraviolet, visible,

and infrared performance. The successful design incorporates a silver reflective layer with a copper underlayer and a stack of dielectric overlayers. Prototypes of the candidate coating have been deposited on two-inch glass slides and tested in a controlled environmental chamber and under true operating conditions on Kitt Peak in Arizona. The improved durability, partly due to the copper underlayer, has been investigated with analytical techniques, including Rutherford backscattering. The results showed that the protection of the silver is due not only to the dielectric stack and the copper beneath the layer, but also to a small amount of copper that appears on the outer surface of the silver layer. This surface copper may result from diffusion through the silver layer after the coating deposition, or may be a consequence of a process during film growth. Whatever the reason, the candidate coatings have better optical performance and improved durability so they are recommended for use on large telescope mirrors for astronomical observations in the near ultraviolet, visible, and infrared spectral regions.

CHAPTER 1

INTRODUCTION

The large astronomical telescopes are invariably used over a wide spectral region for a variety of experiments. Although the smaller elements may be changed when the telescope role is altered, the larger elements remain in place. Cost and engineering considerations prohibit the exchanging of the large primary mirror when a different spectral region is to be investigated. Ground-based astronomical observations are made throughout the ultraviolet from around 300 nm to the far infrared in the 8 and 14 μm atmospheric windows. Mirror surfaces are therefore coated so that they reflect well throughout this extensive region.

The coating material that has been universally adopted for use on telescope mirrors is aluminum. Aluminum has high reflectance throughout the infrared, visible and ultraviolet with a small dip in the near infrared. It is very reactive but the thin oxide layer that form on the surface passivates it and affects the reflectance only slightly. It gives coatings of high quality even when deposited at room temperature and this is a considerable advantage because the large primary mirrors must not be heated during deposition. As with all metallic coatings only a thin layer, 100 nm or less in geometrical thickness, is required to give a reflectance comparable with the bulk metal. Uniformity of this coating does not present any major problems. Multiple sources, often arranged in a ring, are usually sufficient to achieve more than

satisfactory uniformity.

In spite of the very high reflectance of metals in the infrared, nevertheless there are some losses that can be translated into an emissivity can not be neglected. In particular, infrared astronomical observations can be severely limited by the radiation emitted by the reflecting surfaces of the telescope optics. Since the signal is collected and directed toward the detector by these surfaces, the radiation that they emit in the wavelength band being observed cannot be prevented from reaching the detector along with the desired signal. The detection limit could be significantly improved if the unwanted radiation were reduced. This might be accomplished by cooling the entire structure or by chopping the signal at the entrance aperture, but the most practical solution for a large telescope is to reduce the mirror emissivity by improving the reflective coatings.

Telescope mirrors used over a broad spectral range are usually coated with aluminum, which has high reflectance throughout the ultraviolet, visible, and infrared regions. A further requirement is that the mirror not require heating during deposition to improve coating quality; aluminum also performs well in this respect. However, although its emissivity is low in the infrared, it is nevertheless high enough to generate significant infrared background. Since there are only several metals which can compare with aluminum in terms of their optical performance and infrared emissivity, we will discuss the characteristics of aluminum, silver, and gold only.

The measured normal emissivities of some metals are given in Table 1, which is extracted from the Infrared Handbook. One can see from the table that the total normal emissivity of silver and gold are smaller than that of aluminum. However, we are interested in the infrared emissivity rather than the total normal emissivity, which is measured over the whole spectral range, and so we calculate the spectral emissivity of these metals at certain wavelength such that we can compare aluminum with them. The theoretical normal spectral emissivity for a metal with optical constants of $n-ik$ in a medium of index n_0 is

$$\frac{4n_0n}{(n_0+n)^2+k^2} \cdot \quad (1.1)$$

This equation is based on the assumption that

$$E(\lambda) \approx A(\lambda) \approx 1-R(\lambda) \quad (1.2)$$

where E is the emissivity, A the absorptance, and R the reflectance of the metal. The published optical constants of aluminum, silver, and gold have been used to calculate the emissivity at 6 and 10 μm shown in Table 2.

Gold resists corrosion better than silver, and would be the best choice if it were not for its poor visible and ultraviolet performance. Since few telescopes are dedicated to infrared astronomy, coatings must

Table 1. Measured normal emissivity over the entire spectrum for aluminum, copper, and silver.

Material	Temperature	Total Normal Emissivity
Aluminum (vacuum deposition)	20° C	0.04
Aluminum (heavily oxidized)	100° C	0.20
Copper (polished)	100° C	0.05
Silver (polished)	100° C	0.03
Gold (polished)	100° C	0.02

Table 2.   Calculated normal spectral emissivity at 6 and 10 μm are shown for aluminum, gold, and silver. The optical constants were obtained from Hass and Hadley, American Institute of Physics Handbook; those for gold refer to bulk rather than thin film form.

	6 μm		10 μm	
	n-ik	Emissivity	n-ik	Emissivity
Aluminum	10.8-148.56	0.0221	26.0-167.3	0.0198
Gold	4.7-135.2	0.0148	11.5-167.5	0.00976
Silver	4.15-142.6	0.0090	10.69-169.0	0.00873

also reflect well in the visible and ultraviolet. Silver has marginally better performance than gold in the infrared, but has much better visible reflectance; despite its inferiority in durability, it is the first choice. Its ultraviolet reflectance, unfortunately, is low. Figure 1.1 shows a comparison between aluminum and silver coatings in the ultraviolet and visible.

Experiments at Kitt Peak National Observatory on an infrared telescope primary coated with sapphire-protected silver have shown that the optical performance offers a considerable improvement over aluminum. Unfortunately, the sapphire was found to offer insufficient environmental protection, and the coating degraded to the point where it had to be removed after only ten months of use. The corrosion proceeded as an array of growing moisture penetration patches, often encountered in coated optics exposed to the atmosphere (see Figure 1.2).

There are two principal problems with silver: the low ultraviolet reflectance that falls virtually to zero in the 300-320 nm region, and the poor environmental resistance. Both of these problems must be solved to create a qualified silver-based coating. The dissertation describes the progress towards these goals.

Organization of the Dissertation

Chapter 2 develops the basic theory for the design of the high-reflectance boosting coating, and for the analysis of the surface plasmon on a metal. Chapter 3 describes the initial approach to the silver based coating where the principal idea of the coating design is based on the theory in Chapter 2. The phase changes over the mirror

Fig. 1.1 Comparison of reflectance between aluminum and silver in the ultraviolet and visible region.

Fig. 1.2 A photograph of the 1.2 M primary mirror of the infrared telescope showing the progress of the corrosion after 10 months of service.

surface and the tolerances on the layer thickness are discussed in Chapter 4, where we will show that the candidate coating designs are acceptable in terms of the maximum wavefront errors, and then the thickness-monitoring techniques are described for the manufacture of the coatings. Chapter 5 measures the durability of the candidate coatings and introduces the silver-based coating with a copper underlayer that greatly improves the durability. In the last section of this chapter we will discuss the surface plasmon resonance that can be seen in the optical performance of the silver-based coating. Several techniques for the analysis of the silver-copper coating are investigated in Chapter 6 and lead to a model for its durability improvement. Chapter 7 describes the results of field testing of the candidate coatings. Samples, along with a variety of other coatings including plain silver, and silver overcoated with sapphire have been exposed on the 4 meter telescope on Kitt Peak for over one year. Finally, a summary of this study and a discussion of some remaining problems in depositing the candidate coating on large telescope mirrors will be discussed in Chapter 8.

CHAPTER 2

BASIC THEORY

The purpose of this chapter is to set up the basic theory for the design of the high-reflectance mirror coating, and for the analysis of the resonance associated with a surface plasmon in the silver-based coating. The basic theory used for the design follows the derivation in Macleod's book (1969) and his class notes at the Optical Sciences Center. The notes here are not intended to be a complete derivation of the theory but simply recall important results and establish a notation. The basic theory for the surface plasmon at a metal surface will be derived following the dissertation of Yves J. Chabal (1980), although the theory was first shown theoretically by Ritchie in 1957.

The Characteristic Matrix of a Thin Film

The basic technique for thin-film calculation involves the electric and magnetic fields in the thin-film stack. Basically, the development proceeds as follows: consider an incident plane wave which is represented as

$$E(z,t) = E_0 \exp \left[i \left(\omega t - \frac{2\pi z}{\lambda} \right) \right] \quad (2.1)$$

where $E(z,t)$ is the electric field amplitude, E_0 a constant complex

vector, ω the angular frequency of the plane wave, and λ the wavelength in the medium. Here we have assumed the incident wave propagates along positive z direction, so we now consider the electric field normal to the z -direction in, say, the x -direction at time t corresponding to linearly polarized light. However, we conventionally express the field in terms of the wavelength in vacuum. Then the equation (2.1) becomes

$$E_x(z,t) = E_0 \exp \left[i \left(\omega t - \frac{2\pi N z}{\lambda} \right) \right] \quad (2.2)$$

where N is the complex refractive index of the medium ($N=n-ik$, n and k being real), and λ now the wavelength of the propagating wave in vacuum.

The magnetic field can be calculated from the electric field by

:

$$H_y = y E_x \quad (2.3)$$

where y is the admittance of the medium and is equal to the complex refractive index N times the admittance of free space Y_0 , provided the relative magnetic permeability is approximately unity (this is the case in the optical region). In much of our work we will be interested in the ratios of quantities rather than absolute values. Such results are unaffected by the absolute values of optical admittance and depend only on the ratios. There is an advantage in having optical admittance numerically equal to the refractive index. We can do this by expressing

y in SI units of the admittance of free space. In "free space units," then, the optical admittance is given by :

$$Y = n - ik \text{ free space units.} \quad (2.4)$$

The effect of the plane-parallel interfaces in the thin film stack is only to give rise to forward and backward running waves. We apply the boundary conditions, which are that components of electric and magnetic fields that are parallel to the boundary are continuous across it. The fields at the interface are

$$E_a = E^+_{0a} + E^-_{0a} = E^+_{1a} \quad (2.5)$$

$$H_a = H^+_{0a} - H^-_{0a} = H^+_{1a} \quad (2.6)$$

where subscript a indicates the interface a, superscripts + or - denote the wave along the direction of incident or against it, subscripts 0 or 1 denote the particular side of the interface, and H is the magnetic field. Similarly, the fields at interface b are

$$E_b = E^+_{1b} + E^-_{1b} = E^+_{1b} \quad (2.7)$$

$$H_b = H^+_{1b} - H^-_{1b} = H^+_{1b} . \quad (2.8)$$

However, the total fields are affected by the propagation of the positive and negative going components between interfaces a and b (see Figure 2.1). There are

Fig. 2.1 Schematic drawing of a single layer, with forward and backward travelling waves.

$$E^+_{1a} = E^+_{1b} \exp(i\delta) \quad (2.9)$$

$$H^+_{1a} = H^+_{1b} \exp(i\delta) \quad (2.10)$$

$$E^-_{1a} = E^-_{1b} \exp(-i\delta) \quad (2.11)$$

$$H^-_{1a} = H^-_{1b} \exp(-i\delta) \quad (2.12)$$

where

$$\delta = 2\pi N d, \quad (2.13)$$

d being the geometric thickness between interface a and b . Therefore, the electric and magnetic fields which are just across the interface a can be obtained from

$$E_a = E^+_{1a} + E^-_{1a} = E_b \cos \delta + i \sin \delta \frac{H_b}{y} \quad (2.14)$$

$$H_a = H^+_{1a} - H^-_{1a} = i y \sin \delta E_b + \cos \delta H_b. \quad (2.15)$$

This may be combined in the matrix form :

$$\begin{bmatrix} E_a \\ H_a \end{bmatrix} = \begin{bmatrix} \cos \delta & i \sin \delta / y \\ i y \sin \delta & \cos \delta \end{bmatrix} \begin{bmatrix} E_b \\ H_b \end{bmatrix}. \quad (2.16)$$

It is usually expressed in a normalized form:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{bmatrix} \cos \delta & i \sin \delta / y \\ i y \sin \delta & \cos \delta \end{bmatrix} \begin{bmatrix} 1 \\ Y_s \end{bmatrix} \quad (2.17)$$

where Y_s is the admittance of the substrate, that is the ratio of magnetic field and electric fields in the substrate, B and C correspond to the electric and magnetic field across the interface of the thin film, and the equivalent admittance of the assembly is

$$Y = \frac{C}{B} . \quad (2.18)$$

The total field may be computed at any plane in the system by recursively applying equation (2.16), beginning at the substrate and proceeding backwards through the system. In addition, we can also calculate the coefficients of amplitude reflection and transmission from equation (2.17), which are

$$\rho = \frac{Y_0 B - C}{Y_0 B + C} \quad (2.19)$$

$$\tau = \frac{2Y_0 B}{Y_0 B + C} \quad (2.20)$$

where ρ is the amplitude reflection coefficient, τ the amplitude transmission coefficient, and Y_0 the admittance of the incident medium, which must be real to satisfy the relation $1=T+R$ for dielectric systems. The reflectance is then given by

$$R = \rho \rho^* \quad (2.21)$$

where $*$ indicates the complex conjugate. Since the coating may not be

$$R = \rho \rho^* \quad (2.21)$$

where * indicates the complex conjugate. Since the coating may not be absorption free, $T=1-R-A$ (A is the absorptance), is more correct. Then the transmittance is slightly more complicated and we need to introduce the concept of potential transmission in order to calculate it.

Potential transmission is the ratio of the intensity emerging from multilayer and the intensity entering the multilayer from the incident medium, which can be represented as

$$\psi = \frac{I_0 T}{I_0(1-R)} = \frac{\text{Intensity emerging}}{\text{Intensity entering}} = \frac{\text{Re}(Y_S)}{\text{Re}(BC^*)} \quad (2.22)$$

where I_0 is the total intensity from incident medium, and Y_S the admittance of substrate. So now the transmittance is

$$T = \frac{(1-R)\text{Re}(Y_S)}{\text{Re}(BC^*)} = \frac{4Y_0\text{Re}(Y_S)}{(Y_0B+C)(Y_0B+C)^*} \quad (2.23)$$

Effect of Angle of Incidence

The optical phase thickness of thin films becomes thinner as the film is tilted or as the incident light enters the system at an angle, so that the characteristics of the coating move toward shorter wavelengths. However, in order to calculate the optical performance of thin films in the case of oblique incidence, we have to modify the theory described in

the last section. First of all, we must base our definitions of quantities on the components of the fields which are parallel to, and intensities which are normal to, the interface, because only the intensities which are normal to the interface are constant through the system. Second, we must split the waves into two components, one with electric vector parallel to the plane of incidence, known as p-polarized light, and one with electric vector perpendicular to the plane of incidence, known as s-polarized light. These two cases are solved separately and the final results simply involves the combination of the two solutions. We must also redefine optical admittance as the ratio of the components of magnetic and electric field parallel to the interfaces, and it then becomes different for the two planes of polarization. The analysis is, in fact, straightforward, the major complication being this use of two separate values for the optical admittance, s-polarized and p-polarized.

For s-polarization, the optical admittance at θ_0 incidence is

$$\eta_s = \frac{H \cos \theta}{E} = Y \cos \theta \quad (2.24)$$

where θ is given by Snell's law. For p-polarization, the optical admittance at θ_0 incidence is

$$\eta_p = \frac{H}{E \cos \theta} = \frac{Y}{\cos \theta} , \quad (2.25)$$

and the phase thickness of the layers becomes for each plane of polarization,

$$\delta = \frac{2\pi(n-ik)d}{\lambda} \cos\theta . \quad (2.26)$$

The equations from (2.17) to (2.23) can now be applied to calculate reflectance and transmittance for p and s-polarized light, but the optical admittances are η_p or η_s at oblique incidence instead of Y at normal incidence, and also the phase thickness is reduced by a factor of $\cos\theta$. Thus the optical performance varies when the incident angle changes.

For a high-reflectance coating, as the incident angle increases, the reflectance band for p-polarization tends to shrink and s-polarization to widen. The bandwidth is proportional to the ratio of the indices of high and low-index layer, and the values of the ratio of p and s-polarizations are now

$$\left(\frac{\eta_h}{\eta_l}\right)_p = \frac{Y_h \cos\theta_h}{Y_l \cos\theta_l} \leq \left(\frac{Y_h}{Y_l}\right) \quad (2.27)$$

$$\left(\frac{\eta_h}{\eta_l}\right)_s = \frac{Y_h \cos\theta_l}{Y_l \cos\theta_h} \geq \left(\frac{Y_h}{Y_l}\right) . \quad (2.28)$$

However, the total optical performance is the average of the performances of the two polarizations at a given incident angle, so the effects of angle are to reduce the reflectance somewhat and shift the characteristics toward shorter wavelength because of the reduced phase

thickness.

Boosted Reflectance of a Metal

The amplitude reflectance of an assembly is

$$\rho = \frac{y_0 - (\frac{C}{B})}{y_0 + (\frac{C}{B})}$$

where y_0 is the admittance of the incident medium, The reflectance is

$$R = \rho \rho^* ,$$

where * indicates the complex conjugate. For a metal with a characteristic admittance $n-ik$, the reflectance in air at normal incidence is

$$R = \left[\frac{1-(n-ik)}{1+(n-ik)} \right] \left[\frac{1-(n-ik)}{1+(n-ik)} \right]^*$$

i.e.

$$R = \frac{k^2 + (1-n)^2}{k^2 + (1+n)^2} . \quad (2.29)$$

From equations (2.17) and (2.18) the admittance of an assembly , Y , becomes $(\frac{Y^2}{Y})$ or $(\frac{n^2}{Y})$ when a quarterwave optical thickness of index n is added.

If the metal is overcoated with two quarterwaves of material of indices n_1 and n_2 , n_2 being next to the metal, then the optical admittance at normal incidence is

$$Y = \left(\frac{n_1}{n_2}\right)^2(n-ik)$$

according to quarterwave rule, and then the reflectance in air is

$$R = \left(\frac{y_0 - Y}{y_0 + Y}\right)\left(\frac{y_0 - Y}{y_0 + Y}\right)^* \quad (2.30)$$

i.e.

$$R = \frac{1 - \frac{2n\left(\frac{n_1}{n_2}\right)^2}{1 + (n^2 + k^2)\left(\frac{n_1}{n_2}\right)^4}}{1 + \frac{2n\left(\frac{n_1}{n_2}\right)^2}{1 + (n^2 + k^2)\left(\frac{n_1}{n_2}\right)^4}} \quad .$$

This will be greater than the reflectance of the bare metal if

$$\left(\frac{n_1}{n_2}\right)^2 > 1$$

or

$$\left(\frac{n_1}{n_2}\right)^2 < \frac{1}{n^2 + k^2}$$

assuming that n^2+k^2 is greater than unity. The first solution is of greater practical value than the second, which can be ignored. This shows that the reflectance of any metal can be boosted by adding a pair of quarterwave layers for which $(\frac{n_1}{n_2}) > 1$, n_1 being on the outside and n_2 next to the metal. The higher this ratio, the greater the increase in reflectance.

Admittance Diagram

Although the calculation by computer of multilayer coating properties is now rapid and efficient, some graphical techniques are still useful in design and in visualization of coating performance. Admittance loci is one such graphical technique. Since no approximations except in the accuracy of drawing are involved, it can be used in conjunction with computer analysis to yield a very powerful and accurate method.

In an Argand diagram, we plot the locus of the optical admittance of a multilayer measured at a notional surface, parallel to the substrate, which is swept through each layer, starting at the substrate and ending at the front surface. It is as if we plotted the admittance of the multilayer during the entire deposition process. For each dielectric layer, the locus is an arc of a circle centered on the real axis. For metallic layers the locus is a more complicated spiral. Here we consider the dielectric layers first.

We measure Y in free space units and assume that we have one single layer of admittance n on a substrate of admittance $\alpha + i\beta$. Then

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{bmatrix} \cos\delta & i\sin\delta/n \\ i\sin\delta & \cos\delta \end{bmatrix} \begin{bmatrix} 1 \\ \alpha + i\beta \end{bmatrix} \quad (2.31)$$

where δ is a variable of the form

$$\delta = \frac{2\pi nd}{\lambda}$$

and

$$Y = \frac{C}{B} .$$

Y will in general be complex, of the form $a+ib$, and we can then write :

$$Y = a + ib = \frac{\alpha \cos\delta + i(\frac{\sin\delta}{n} + \beta \cos\delta)}{(\cos\delta - n\beta \sin\delta) + i n\alpha \sin\delta} . \quad (2.32)$$

We separate real and imaginary parts

$$\begin{aligned} a(\cos\delta - \frac{\beta \sin\delta}{n}) - \frac{b\alpha \sin\delta}{n} &= \alpha \cos\delta \\ b(\cos\delta - \frac{\beta \sin\delta}{n}) + \frac{a\alpha \sin\delta}{n} &= (n\sin\delta + \beta \cos\delta) \end{aligned}$$

and eliminate δ to give the equation of the admittance locus:

$$a^2 + b^2 - \frac{a(n^2 + \alpha^2 + \beta^2)}{\alpha} + n^2 = 0 . \quad (2.33)$$

$$a^2 + b^2 - \frac{a(n^2 + \alpha^2 + \beta^2)}{\alpha} + n^2 = 0 . \quad (2.33)$$

i.e. a circle with center $(\frac{n^2 + \alpha^2 + \beta^2}{2\alpha}, 0)$ passing through the point (α, β) .

For the loci of constant δ , phase thickness, we assume that β is zero and then eliminate α giving

$$a^2 + b^2 + bn(\frac{1}{\tan\delta} - \tan\delta) - n^2 = 0 . \quad (2.34)$$

i.e. a circle with center $(0, \frac{n(\tan\delta - \frac{1}{\tan\delta})}{2})$, that is, on the imaginary axis, passing through the point $(n, 0)$. (see Figure 2.2)

The circle is traced out clockwise. If the starting point is on the real axis, then a semicircle corresponds to a quarterwave. Drawing the circle becomes easy if we note that, if one point of intersection with the real axis is given by α , then the other point of intersection will be $\frac{n^2}{\alpha}$.

In a similar way we can plot isorefectance contours on the same diagram. There are circles which are also centered on the real axis.

Their centers are given by $(\frac{n(1+R)}{1-R}, 0)$ and their radii by $\frac{2n\sqrt{R}}{1-R}$, where n is the admittance of the incident medium. (see Figure 2.3)

Isophase contours, that is the phase change on reflection, can also be added. The most important are the boundaries between the various quadrants. These are the real axis and the circle with center

Fig. 2.2 Admittance diagram showing the locus of a single layer with refractive index of n .

Fig. 2.3 Admittance diagram with isophase contours and isorefectance contours.

the origin passing through the point $(n_0, 0)$ (see Figure 2.3) where n_0 is the index of the incident medium.

Metal layers or other absorbing layers require the assistance of a computer. As $n-ik$ tends to $-ik$, i.e. as n tends to zero, the locus tends to a circle centered on the real axis passing through the point $(0, -k)$ and traced out clockwise. For $n \neq 0$, but n very small, the loci are similar to this set of circles but now passing through the points $n-ik$ and $-n+ik$. For large n , the loci become spirals tending towards $n-ik$ as their thickness increases.

Overcoats

For the case of $n \neq 0$, a circular locus which passes through the point of $n-ik$ and is centered on the real axis, represents an overcoating dielectric layer. The lower the index, the closer the point of intersection with the real axis is to the origin and the larger the corresponding reflectance if the optical thickness is between quarter and $\frac{1}{8}$ th wave (see Figure 2.4). This indicates that in order to have highest reflectance, the layer next to the metal should be of low index. Subsequent layers should be high-index and low-index layer alternately.

The admittance locus of a four-layer reflectance boosting coating deposited over silver is plotted in Figure 2.4 and Figure 2.5. Here we are interested in the ultraviolet at a wavelength of 300 nm. Figure 2.4 shows the locus starts at silver of index $1.67-i0.96$ and ending at the surface of the outermost layer where the first layer is a 0.2 wavelengths of Al_2O_3 , with index of 1.694 ending virtually on the real

IMAGINARY ADMITTANCE

TA2O5/SiO2/TA2O5/0.8AL2O3/Ag

Fig. 2.4 Admittance locus of a boosting coating over silver. The design is $Air|Ta_2O_5|SiO_2|Ta_2O_5|(0.8)Al_2O_3|Ag$ at reference wavelength 300 nm.

axis. The second layer is a quarterwave of Ta_2O_5 , with index of $2.5-i0.004$, the third layer is a quarterwave of SiO_2 , with index of 1.463 , and the last layer is the same as the second layer. The reference wavelength of this design is 300 nm . Figure 2.5 shows the same design as in Figure 2.4 but plots the locus at a wavelength of 320 nm . As one can see in the diagram the locus shrinks because the optical thickness is reduced by a factor of $\frac{15}{16}$. In addition, the indices of the layers are different because the wavelength has changed. However, even at this second wavelength, the equivalent admittance is now located at a higher isorelectance contour than for uncoated silver, so that the reflectance in the near ultraviolet is greatly increased by the four-layer boosting stack.

Electric Field Distribution in the Multilayer Coating

A further advantage of the admittance locus beyond the obvious visualization of performance, is that contours of electric field amplitude, of importance in laser damage performance and in phenomena such as the coupling into surface plasmons, are very simple in form, and can readily be added when all the layers are dielectric. We assume the admittance is in free space units as usual and so we will introduce Y_0 as a correction factor so that E is given in $\frac{\text{volts}}{\text{meter}}$. We can write for the net intensity passing into the multilayer,

$$\frac{1}{2} Y_0 \operatorname{Re}(BC^*) = \frac{1}{2} Y_0 \operatorname{Re}(YBB^*) = \frac{1}{2} Y_0 BB^* \operatorname{Re}(Y) \quad (2.35)$$

IMAGINARY ADMITTANCE

TA205/SI02/TA205/0.8AL203/AG

Fig. 2.5 Admittance locus of a boosting coating over silver with the same design as in Fig. 2.4 but reference wavelength at 320 nm.

where Y_0 = admittance of free space = $\frac{1}{377}$ Siemens, and Y is in free space units. Further,

$$BB^* = E^2 = (\text{electric field amplitude})^2 .$$

Now, when the layers are dielectric the net intensity actually entering the assembly is the same as that which emerges. Let unit intensity emerge from the multilayer system. Then

$$E^2 = BB^* = \frac{1}{Y_0 \frac{\text{Re}(Y)}{2}} = \frac{754}{\text{Re}(Y)} . \quad (2.36)$$

If the incident intensity is unity, then

$$E = \frac{27.46 \sqrt{T}}{\sqrt{\text{Re}(Y)}} \quad (2.37)$$

where T is the transmittance. E is in $\frac{\text{volts}}{\text{meter}}$ provided that Y is in free space units. (i.e. if Y is numerically equal to refractive index.) So the electric field is decreasing as the optical admittance of the assembly is increasing (see Figure 2.6). The form of the E -contours is a set of parallel lines which are all perpendicular to the real axis. The closer they are to the imaginary axis, the higher the electrical field. For a circular contour in the admittance diagram (for most multilayer

Fig. 2.6 Electric field contours on an admittance diagram.

coatings), the electric field oscillates as the admittance moves round the locus. This gives a sinusoidal variation of the electrical field inside the coating.

Surface Plasmons at a Metal Surface

Surface plasmons are quanta of energy of surface electromagnetic waves, which are inhomogeneous electromagnetic modes propagating in a wave-like manner along the interface between two media. These surface modes, involving photons coupled to surface electric dipole excitations, are often called alternatively surface polaritons. Their existence was appreciated by Zenneck (1907) and Sommerfeld (1909) who showed that radio frequency surface electromagnetic waves occur at the boundary of two media when one medium is either a lossy dielectric or a metal and the other is a loss-free medium. These investigators showed that it is the imaginary part of the dielectric constant ($2n_k$) which is necessary for the binding of the electromagnetic wave to the interface. The existence of surface plasmons at a metal surface was first shown theoretically by Ritchie (1957).

We now present the classical derivation of a surface electromagnetic wave in terms of the characteristic quantities (fields, wavevectors). Consider the interface between a metal and a dielectric as shown in Figure 2.7. The dielectric occupies the upper half space ($z < 0$) and the metal the lower half space ($z > 0$). The interface response to an electromagnetic perturbation is characterized by the dielectric constants of the two media: $\epsilon_d(\omega)$ and $\epsilon_m(\omega)$ for the dielectric and metal respectively. We assume that both permeabilities are unity.

Fig. 2.7 Schematic drawing of the metal-dielectric interface.

We are looking for solutions to Maxwell's equations subject to the boundary conditions that the components of electric and magnetic fields that are parallel to the boundary are continuous across it. For a TM mode, the magnetic field lies parallel to the surface, and is given by

$$H(r, t) = H_0 (0, 1, 0) \exp[i(\omega t - k_x x - k_z z)] , \quad (2.38)$$

where $(0, 1, 0)$ is a unit vector along the y -direction. The boundary condition, H continuous everywhere on the surface ($z=0$), shows that in both media H_0 and k_x are equal. We can then write the fields in the dielectric

$$H_d(r, t) = H_0 (0, 1, 0) \exp[i(\omega t - k_x x - k_d z)] \quad (2.39)$$

and from Maxwell's equation $\frac{\partial D}{\partial t} = \epsilon \frac{\partial E}{\partial t} = c \nabla \times H$ we obtain

$$E_d(r, t) = \frac{c}{i\omega\epsilon_d} \nabla \times H_d(r, t)$$

ie.

$$E_d(r, t) = \frac{c}{\omega\epsilon_d} H_0 (-k_d z, 0, -k_x) \exp[i(\omega t - k_x x + k_d z)] \quad (2.40)$$

for $z < 0$, where the dielectric constant of the dielectric medium, ϵ_d , is a function of frequency, and $k_d z$ is the wave vector along the z -direction

in the dielectric medium. In the metal

$$H_m(r, t) = H_0 (0, 1, 0) \exp[i(\omega t - k_x x - k_{mz} z)] \quad (2.41)$$

$$E_m(r, t) = \frac{c}{\omega \epsilon_m} H_0 (k_{mz}, 0, -k_x) \exp[i(\omega t - k_x x - k_{mz} z)] \quad (2.42)$$

for $z > 0$, where the dielectric constant of the metal ϵ_m is also a function of frequency, and k_{mz} is the wave vector along the z -direction in the metal.

The condition that the component of electric field parallel to the boundary is also continuous across it, yields immediately the relation

$$\frac{k_{dz}}{\epsilon_d}(\omega) = -\frac{k_{mz}}{\epsilon_m}(\omega) \quad (2.43)$$

This equation shows that the surface electromagnetic wave will decay exponentially into both media, i.e. $\text{Im}(k_{dz}) < 0$ and $\text{Im}(k_{mz}) < 0$, only if

$$\text{Re}[\epsilon_m(\omega)] \leq -\text{Re}[\epsilon_d(\omega)] . \quad (2.44)$$

However, $\text{Re}[\epsilon_d(\omega)] = n^2 - k^2$ is positive for all dielectrics, and so equation (2.44) may be satisfied only if $\text{Re}[\epsilon_m(\omega)]$ is negative. This is true for silver in the visible and infrared region, and for all metals in the infrared range. Substituting equations (2.39) and (2.41) into the wave

equations:

$$\nabla^2 H_d - \frac{\epsilon_d}{c^2} \partial^2 \frac{H_d}{\partial t^2} = 0 \quad (2.45)$$

$$\nabla^2 H_m - \frac{\epsilon_m}{c^2} \partial^2 \frac{H_d}{\partial t^2} = 0 , \quad (2.46)$$

we have

$$k_x^2 + k_{dz}^2 = \epsilon_d \left(\frac{\omega}{c}\right)^2 \quad (2.47)$$

$$k_x^2 + k_{mz}^2 = \epsilon_m \left(\frac{\omega}{c}\right)^2 .$$

Combining equations (2.43) and (2.47), we obtain

$$k_x = \left(\frac{\omega}{c}\right) \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} . \quad (2.48)$$

This is the dispersion relation for surface electromagnetic waves and was first derived by Ferrell in 1956. The real part, k_{x1} , describes the oscillation frequency of the surface electromagnetic wave and the imaginary part, k_{x2} , gives its absorption by the metal. The absorption coefficient is defined as

$$\alpha(\omega) = \frac{1}{2k_{x2}(\omega)} . \quad (2.49)$$

From equations (2.47) and (2.48), we can calculate the perpendicular components of the surface electromagnetic wave

$$k_{dz} = \left(\frac{\omega}{c}\right) \epsilon_d(\omega) \frac{1}{\sqrt{\epsilon_d + \epsilon_m}} \quad (2.50)$$

$$k_{mz} = \left(\frac{\omega}{c}\right) \epsilon_m(\omega) \frac{1}{\sqrt{\epsilon_d + \epsilon_m}} . \quad (2.51)$$

The real parts of these wavevectors show the change in phase which occurs in a decay length, and the imaginary parts determine the decay length into both media.

The general solutions for k_{x1} and k_{x2} are obtained after separating real and imaginary parts in equation (2.48) :

$$k_{x1} = \left(\frac{\omega}{c}\right) \sqrt{\left(\frac{1}{2D}\right)(A + \sqrt{A^2 + B^2})} \quad (2.52)$$

$$k_{x2} = \left(\frac{\omega}{c}\right) \left(\frac{B}{2D}\right) \frac{1}{\sqrt{\left(\frac{1}{2D}\right)(A + \sqrt{A^2 + B^2})}} \quad (2.53)$$

where

$$A = \epsilon_{d1} (\epsilon_{m1}^2 + \epsilon_{m2}^2) + \epsilon_{m1} (\epsilon_{d1}^2 + \epsilon_{d2}^2)$$

$$B = \epsilon_{d2} (\epsilon_{m1}^2 + \epsilon_{m2}^2) + \epsilon_{m2} (\epsilon_{d1}^2 + \epsilon_{d2}^2)$$

$$C = (\epsilon_{m1} + \epsilon_{d1})^2 + (\epsilon_{m2} + \epsilon_{d2})^2$$

$$\epsilon_d = \epsilon_{d1} + i\epsilon_{d2}$$

$$\epsilon_m = \epsilon_{m1} + i\epsilon_{m2} .$$

These relations can be simplified if $\epsilon_{d2} = 0$ and $|\epsilon_{m1}|, \epsilon_{m2} \gg \epsilon_{d1} \geq 1$.

The assumptions are true for metals and dielectrics in infrared region.

So

$$k_{x1} \approx \left(\frac{\omega}{c}\right) \sqrt{\epsilon_{d1}} \left(1 - \left(\frac{3}{4}\right) \frac{\epsilon_{m1} \epsilon_{d1}}{\epsilon_{m1}^2 + \epsilon_{m2}^2}\right) \quad (2.54)$$

$$k_{x2} \approx \left(\frac{\omega}{c}\right) \epsilon_{d1} \sqrt{\epsilon_{d1}} \left(\frac{\epsilon_{m2}}{2(\epsilon_{m1}^2 + \epsilon_{m2}^2)}\right) \quad (2.55)$$

$$k_{dz1} \approx -\left(\frac{\omega}{c}\right) \epsilon_{d1} \sqrt{\frac{\epsilon_{m1} + \sqrt{\epsilon_{m1}^2 + \epsilon_{m2}^2}}{2(\epsilon_{m1}^2 + \epsilon_{m2}^2)}} \quad (2.56)$$

$$k_{dz2} \approx \left(\frac{\omega}{c}\right) \epsilon_{d1} \sqrt{\frac{-\epsilon_{m1} + \sqrt{\epsilon_{m1}^2 + \epsilon_{m2}^2}}{2(\epsilon_{m1}^2 + \epsilon_{m2}^2)}} \quad (2.57)$$

$$k_{mz1} \approx -\left(\frac{\omega}{c}\right) \sqrt{\frac{\epsilon_{m1} + \sqrt{\epsilon_{m1}^2 + \epsilon_{m2}^2}}{2}} \quad (2.58)$$

$$k_{mz2} \approx \left(\frac{\omega}{c}\right) \sqrt{\frac{-\epsilon_{m1} + \sqrt{\epsilon_{m1}^2 + \epsilon_{m2}^2}}{2}} . \quad (2.59)$$

These equations, except k_{x1} , are derived up to order $\frac{1}{\epsilon_m}$ which is well

satisfied in the near IR and IR regions. k_{x1} was derived up to order

$\frac{1}{(\epsilon_m)^2}$ in order to permit comparison with the free space wavevector, $\left(\frac{\omega}{c}\right)$

$\sqrt{\epsilon_{dl}}$. Since ϵ_{ml} is negative in the visible and infrared regions, the wavevector of the surface electromagnetic wave is always larger than the free space wavevector. Hence, surface electromagnetic waves can not couple directly to free space. This implies that light incident on a plane metal surface can not couple to a surface plasmon.

For the TE mode, where the electric field is parallel to the surface, the electric field is along the y-direction if a wave is propagating in the x-direction. Following a derivation similar to the above, we can see the conditions of $\text{Im}(k_{dz}) < 0$ and $\text{Im}(k_{mz}) < 0$ can not be satisfied simultaneously for any value of ϵ_m , i.e. no surface wave can be bound to the surface. Physically, this is due to the fact that no net dipole can be induced parallel to the surface due to the complete translational symmetry along the surface. Thus there can be no surface plasmon for TE polarization.

Light Coupling to Surface Plasmons

Almost all the thin films made by the method of vacuum evaporation present a columnar structure and a rough surface. This rough surface can scatter part of the incident light as much as 1 %, and the magnitude of the scattering loss is mainly dependent on the roughness of the film surface. However, the scattering loss can be significantly increased if the incident light couples to surface plasmons.

From the last section, we see that a surface plasmon has a larger wave vector k than that of the incident light. So to couple a

surface plasmon into a metal surface, we need a rough surface to scatter some of the incident light, and make the total wave vector of scattering and incident light equal to that of surface plasmons. The rougher the surface, the stronger the coupling effect. However, the surface plasmons can only occur at the wavelength where the dielectric constant of the metal is negative with absolute values equal to the dielectric constant of the bounded material. Unfortunately, silver is one of the metals that has a surface plasmon in the near ultraviolet region (about 380 nm) if the overcoat is aluminum oxide. Therefore that part of the scattering loss of overcoating on the silver due to the coupling to surface plasmons would be considerable larger than the loss at the other wavelengths. This can degrade the optical performance of the silver boosting coatings in the ultraviolet region.

However, we have found in practice that the coupling is not only dependent on the surface roughness, but also on the field intensity at the metal surface. The addition of more layers on top of aluminum oxide layer may decrease the field intensity at the interface between silver and dielectric stack, and so reduce the effect of the coupling. This implies that the multilayer overcoated silver can have a better optical performance than that of single layer overcoated silver if the electric field intensity is smaller at the interface.

CHAPTER 3

INITIAL APPROACH

We recall our objective of a coating with lower infrared emissivity, yet similar ultraviolet, visible and infrared reflectance to aluminum. There were two possible approaches to an improved coating. An ideal solution would be a metal, or metal alloy, which could simply replace the aluminum with virtually no other changes. An approach based on such a solution, however, would involve a considerable research effort of a fundamental nature with an uncertain outcome, and was clearly impossible within the constraints of the present program. We adopted the more complex but also more certain, conventional thin-film multilayer technique, in which at least part of the performance is achieved by interference. This approach uses existing design techniques and coating technology to advantage, but carries the disadvantage that the solution will require strict thickness uniformity of the layers in interference coatings, rather than the more generous tolerances of single reflecting metal layers.

Theoretical Design

Since silver appears to be optically satisfactory in all regions except the ultraviolet from 300 to 330 nm, it was decided to base the solution on silver and to attempt to correct the deficiency in the ultraviolet. Silver cannot be used unprotected, and some of the

additional layers could also act as passivating layers. Sapphire (Al_2O_3) adheres well to silver and is the preferred material for the first dielectric overlayer. At the beginning, it was believed that sapphire overcoated silver would resist moisture penetration sufficiently, so the initial optical design proceeded on that basis. This view is supported by Lubezky, Ceren, and Klein (1980) , and by Dubkov, and Rozhdestvenskii (1983).

Further, a sapphire overcoat on silver, although it may be as thick as a quarterwave at 600 nm, shows satisfactory infrared emissivity, even though it absorbs strongly beyond $6.5\text{ }\mu\text{m}$. This suggested that a small stack of layers, centered around 300 nm and deposited over silver, might have acceptable infrared emissivity.

Two broad types of coating based on silver have been investigated by Browning, Jacobson, Macleod, Potoff, Song, and Van Milligen (1982): A reflectance-boosting coating over a thick silver layer and a silver coating over aluminum.

Design 1: Reflectance-boosting Coating

The basic high-reflectance all-dielectric multilayer is the quarterwave stack, which consists of alternate high and low-index layers. At the reference wavelength for which all the layers are quarterwaves, all the reflecting interfering beams are in phase and so very high reflectance can be achieved. The introduction of progressive phase errors affects the reflectance strongly only when they become greater than a certain magnitude, so that high reflectance is obtained over a spectral zone, outside of which it falls rapidly. For typical

materials used in the visible and near ultraviolet, the high-reflectance-zone width is several hundred nanometres. Such a dielectric coating can be placed over a metal layer when it boosts the reflectance within the high reflectance zone. Outside the zone, the reflectance falls but except for a narrow dip that can usually be seen at this zone boundary, over the greater part of the region outside this zone, it has a value similar to that of the base metal. Most highly reflecting metals have phase shifts in the 2nd quadrant, so the layer next to the metal should normally be of low index and rather less than a quarterwave in thickness if the phase is to be corrected exactly. However, small phase errors can be neglected, and a quarterwave layer is normally acceptable.

The reflectance boosting coating for the thick silver layer can neither be too thick, increasing the infrared emissivity, nor too thin, decreasing the ultraviolet reflectance. A compromise four-layer overcoating was adopted, the first layer being sapphire, with its low index, followed by a layer of antimony trioxide or tantalum pentoxide, the latter slightly tougher but more difficult to evaporate and control. To boost the reflectance still further, the second low index layer of quartz, of slightly lower index than sapphire, was chosen. Finally, a second antimony trioxide or tantalum pentoxide layer was added. The silver optical constants show rapid dispersion in the 300-330 nm region and there is little to be gained by departing from quarterwave optical thickness for the first low-index layer. However, in this theoretical calculation the value of $0.2 \lambda_0$ was adopted. This gives the design:

Air|H L H M Ag|Glass

with $\text{H-Sb}_2\text{O}_3$, or Ta_2O_5 , L-SiO_2 , $\text{M-Al}_2\text{O}_3$, all quarterwave except the sapphire layer, and with a reference wavelength of 300 nm. The theoretical performance of this design in the ultraviolet, and visible is shown in Figure 3.1(a), and infrared in figure 3.1(b).

Design 2: Silver Overcoat on Aluminum

The second approach involves a thin silver layer over the aluminum, which is thick enough so that the silver dominates in the visible and infrared, but thin enough so that the loss at 300-330 nm does not destroy completely the reflectance of the aluminum in that spectral region. Silver cannot be left as the outermost layer of the assembly, nor should it deposited directly over the aluminum because of possible interdiffusion. Sapphire seems the best diffusion barrier layer as well as the best overcoat. But with sapphire layers on either side of the silver, the reflectance in the 300-330 nm region falls so that a further boosting layer of high index, again either tantalum pentoxide or antimony trioxide, is added.

If the silver layer is too thin, it will be discontinuous with its optical constants shifted considerably from those of a continuous film, so that high reflectance will not be obtained. The minimum thickness limit is around 20 nm and this was the thinnest film assumed in the design calculations. After the silver layer, the most critical layer in the assembly is the barrier layer. Too thick a layer and the reflectance of the aluminum in the ultraviolet is reduced and the phase

Fig. 3.1(a) Calculated reflectances for coating of design : Air | H L H M
Ag | Glass in the visible region.

Fig. 3.1(b) Calculated reflectances for the same coating design as in Fig. 3.1(a) but in the infrared region.

disturbed so much that the overall reflectance becomes unacceptably low. The barrier layer also affects the visible performance, particularly when the silver film is very thin; a thicker barrier layer produces slightly higher reflectance. Trial and error suggested silver should be around 25 nm thick. This reduced the sensitivity of the performance in the visible to the barrier layer thickness and allowed the barrier layer to be made thinner, improving the ultraviolet performance. The sapphire layer over the silver inevitably reduces the reflectance somewhat, but this loss is recovered by adding a further high-index layer. The sapphire overcoat and this outer layer act as a two-layer boosting combination. The final design is:

$$\text{Air} | \text{H M Ag M' Al} | \text{Glass}$$

with H a quarterwave of Ta_2O_5 or Sb_2O_3 , M 0.2 full waves of Al_2O_3 , Ag 25 nm of silver, and M' 0.025 full waves of Al_2O_3 . The reference wavelength is 200 nm which weakens the boosting effect of this coating. Moving this wavelength to 300 nm, however, caused problems at longer wavelength and so 200 nm was retained. The calculated performance of this design is in Figure 3.2.

Experimental Results

In order to simplify the initial problems, the coatings were first attempted with well-known materials. This avoided the difficulties of simultaneously developing techniques for new materials and multilayers of new design. The experimental coatings were produced

Fig. 3.2 Calculated reflectances for coating of design : $\text{Air} \mid \text{H M Ag M}' \mid \text{Al} \mid \text{Glass}$ in the visible region.

by using, as dielectric materials, silicon oxide, cryolite (Na_3AlF_6) and antimony trioxide. Because of the very thin layers involved and because the coating plant is fitted with glass optics, we have monitored film growth with a quartz crystal microbalance originally calibrated with respect to an optical monitor operating in the visible region. The monitoring wavelengths quoted in the results are values calculated from the microbalance signals on the basis of this calibration.

The reflectance of the manufactured coating were measured by a Cary 14 spectrophotometer, which employs a W-type reflectance accessory, capable of absolute measurements with accuracy of 1 %. Since the light is reflected twice by the sample in a W-type reflectance accessory, we actually measure the square of the reflectance rather than the reflectance itself. The other elements in this system have to be eliminated by a further measurement in which the sample is removed and the mirror defining the central peak of the "W" is displaced to make the "W" into a "V". Therefore, we calculate the reflectance by taking the square root of the values, that is the value of the reflectance signal for the coating divided by the reference reflectance signal.

Coating 1: Reflectance-boosting Coating

Figure 3.3 is typical of the attempts to date at the four-layer boosting coating design. The coating was produced to the design:

with the dielectric layers all of quarterwave optical thickness at the

Fig. 3.3 Measured reflectances for coating of design :
 Air | Sb_2O_3 | Na_3AlF_6 | Sb_2O_3 | Si_2O_3 | Ag | Glass.

monitoring wavelength (300 nm) . The thickness of the silver layer was greater than 100 nm which would make the coating opaque in the visible , and near infrared region. The reflectance from 300 to 330 nm is substantially greater than silver but there is a prominent dip around 390 nm which can be as low as 70 % . The dip is due to a resonance involving surface plasmons and has been described by Stanford and Bennett (1969) .

It is interesting to note, also in figure 3.3 the reflectance of silver after only the first silicon oxide layer. This is probably Si_2O_3 , rather than SiO_2 , as it was produced by reactive evaporation of SiO . Si_2O_3 has a higher index than SiO_2 and shows some absorption in the ultraviolet.

Coating 2: Silver Overcoat on Aluminum

The results obtained with the silver overcoat on aluminum are still more promising in optical terms. Again, the design actually produced is slightly different from the theoretical one in that one of the dielectric materials is cryolite. The design is :

The silver layer is approximately 25 nm thick and was monitored optically so that the thickness was just greater than the minimum limit required for film integrity. The barrier layer was produced by admitting oxygen or air to the chamber to form a thin oxide layer on the aluminum.

The reflectance of simple silver overcoated aluminum is shown in Figure 3.4. Clear enhancement of the silver reflectance is obtained.

Fig. 3.4 Measured reflectances of simple silver overcoated aluminum without protection or boosting layers.

The two-layer protecting and boosting combination then lifts the reflectance still further as in Figure 3.5. The effect of increasing slightly the silver layer thickness is also apparent. The reflectance in the 300 to 330 nm region falls while that in the visible region rises.

It is possible that the performance in the 300 to 330 nm region could be further improved by adding further layers but, apart from the increase in complexity of the coating, there is a risk of an adverse effect on the infrared emissivity, since the total dielectric layer thickness would be doubled.

These preliminary results were encouraging and demonstrate that the development of multilayer coatings for astronomical reflectors should lead to improved performance. However, as far as the durability of the coatings was concerned, the tougher materials, such as tantalum pentoxide as high-index layer and silicon dioxide as low-index layer, were also investigated. The coatings that were made using the tougher materials were manufactured satisfactorily with close to theoretical performance. In chapter 5, we will discuss them in more detail.

Fig. 3.5 Measured reflectances of silver overcoated aluminum with two boosting layers.

CHAPTER 4

UNIFORMITY REQUIREMENTS AND TOLERANCES

Given suitable materials, clean substrates, and a plant with substrate holders, the main problems which remain are that of controlling satisfactorily layer thickness and uniformity over the coated surface. In this chapter we will discuss the thickness tolerances, the uniformity requirements, and the monitoring methods of two candidate coatings.

Manufacturing Tolerances

There are no satisfactory analytical techniques for the calculation of manufacturing tolerances and the most useful method is based on Monte Carlo simulation of the manufacturing process. This method was described by Macleod (1977) . Successive simulations with different sets of random errors drawn from the same infinite population, usually normal and with a prescribed mean and standard deviation, are carried out. Inspection of the results which represent the performance which might be expected from successive production batches, permits the assessment of the effects of the errors in terms of performance reduction and process yield. The procedure is repeated with different error characteristics until what is considered to be a satisfactory level of performance and yield is attained. The corresponding magnitude of error is then taken as the tolerance. Although the entire process could

be completely automatic, experience has shown that a visual assessment of the performance curves is more satisfactory. Strictly, the tolerance is not independent of the monitoring method which is to be used in controlling coating production, particularly in respect of systems where the magnitude of our error depends on the thicknesses of previous layers. For broad-band systems it is important usually to choose control systems which ensure that the error in any one layer is completely independent of that in any other, and for such coatings it is sufficient simply to compute the performance of the multilayer with independent random thickness errors in all the layers. This is the technique which has been used in deriving the tolerance figures here.

In terms of tolerances which can be held in a coating plant in normal operation, 10 % should not present any difficulties in a well-maintained plant with standard monitoring facilities, 5 % is a realistic figure which can be achieved with considerable care and attention to detail, while 2 to 3 % is possible only with the greatest care and effort.

The tolerances likely to be required in the manufacture of the two candidate coatings were assessed by this technique. Typical plots are shown in Figures 4.1, 4.2, and 4.3. The performance curves corresponding to 10 % error suggest that this level should be quite satisfactory for the silver overcoat, but slightly less so for the boosting coating, which may require slightly tighter tolerances.

Fig. 4.1 The effect of random thickness errors of 10 % standard deviation on the reflectance boosting coating over silver.

Fig. 4.2 The effect of random thickness errors of 5 % standard deviation on the reflectance boosting coating over silver.

Fig. 4.3 The effect of random thickness errors of 10 % standard deviation on the silver overcoated aluminum.

Coating Uniformity

In addition to the random thickness errors which are used in the calculation of layer thickness tolerances, there are layer thickness errors which are systematic and which arise from a lack of uniformity in the coating plant. Different techniques are used for the calculation of the effects of such errors, and it is usual to assume that all layers of the coating are affected equally.

The immediate effect of uniformity errors is a shift of the characteristic of the coating towards shorter or longer wavelengths, depending on whether the layer thicknesses have decreased or increased. It may be necessary to take dispersion in the materials into account, although this will usually lead to only a very slight distortion of the characteristics, which can be neglected. For most optical coating applications, the shift in the reflectance or transmittance curve is all that needs to be considered, and assessment of uniformity errors and establishment of the requirements for the coating operation are straightforward.

For coatings where wavefront distortion is important, especially reflecting coatings, there is another and potentially much more serious problem which was discussed by Ramsay and Ciddor (1967) . Errors in total coating thickness imply that the surface of the coating is no longer a faithful replica of the substrate surface, and a wavefront error will be introduced in the reflecting light. For opaque metal layers, this wavefront error is twice the thickness error, and since such layers are usually quite thin, reasonably large uniformity errors as a

percentage of total layer thickness can be tolerated. For more complex coatings, interference effects can change the phase of the light reflected by the coating, and if there is a rapid variation of phase with coating thickness then the wavefront error introduced by uniformity errors may be much greater than simple calculations of total coating thickness may indicate.

The total phase change and hence the wavefront error, is thus made up of two components: the part due to the thickness difference, which corresponds to the case of opaque metal films $\frac{2\pi nd}{\lambda}$, and the difference in the phase shifts at the front surfaces of the altered and unaltered multilayers $\Delta\phi = \phi_B - \phi_A$, shown in Figure 4.4.

$$\text{Phase Shift} = \Delta\phi + \frac{4\pi nd}{\lambda} \quad (4.1a)$$

$$\text{Wavefront Error} = \frac{\Delta\phi}{2\pi} + \frac{2nd}{\lambda} . \quad (4.1b)$$

Wavefront errors corresponding to various uniformity errors have been calculated for both candidate coatings as a function of wavelength, and are plotted in Figure 4.5, 4.6, 4.7, and 4.8 in the form of uniformity requirements if wavefront errors introduced by the coating are not to exceed $\frac{\pm\lambda}{20}$ or $\frac{\pm\lambda}{40}$. It is useful to compare these with the requirements for metal layers which were calculated assuming a film thickness of 100 nm. An interesting feature of both coatings is the inherent compensation which exists over wide regions so that the two terms in the wavefront error tend to cancel out. In fact, in both coatings over much of the

$$\text{PHASE SHIFT} = \phi_B - \left[\phi_A - 2 \left(\frac{2\pi nd}{\lambda} \right) \right]$$

$$= (\phi_B - \phi_A) + \frac{4\pi nd}{\lambda}$$

$$= \Delta\phi + \frac{4\pi nd}{\lambda}$$

$$\text{WAVEFRONT ERROR} \quad \frac{\Delta\phi}{2\pi} + \frac{2nd}{\lambda}$$

Fig. 4.4 Diagram showing the origin of the terms in the calculation of the wavefront error resulting from a lack of coating uniformity.

Fig. 4.5 Uniformity requirements for the reflectance boosting coating over silver if the wavefront error is not to exceed $+\frac{\lambda}{40}$ or $+\frac{\lambda}{20}$.

Fig. 4.6 Uniformity requirements for the reflectance boosting coating over silver if the wavefront error is not to exceed $-\frac{\lambda}{40}$ or $-\frac{\lambda}{20}$.

Fig. 4.7 Uniformity requirements for the silver overcoated aluminum if the wavefront error is not to exceed $+\frac{\lambda}{40}$ or $+\frac{\lambda}{20}$.

Fig. 4.8 Uniformity requirements for the silver overcoated aluminum if the wavefront error is not to exceed $-\frac{\lambda}{40}$ or $-\frac{\lambda}{20}$.

region, the wavefront error is opposite in sign to what would be expected from a simple thickness change. The silver overcoat appears superior even to a metal layer, while the boosting overcoat appears less critical than a metal layer over much of its range but at longer wavelengths its uniformity requirement become more severe.

It would be dangerous to conclude from this abbreviated study that the coating uniformity in practice need be no greater than for existing metallic layers, because only one dimension of a multidimensional problem has been considered. But it does suggest that achieving satisfactory uniformity for the multilayer coatings should not present any problems greater than those for normal multilayers.

Monitoring Methods

The quartz-crystal monitor was adopted at the beginning to monitor film growth for reflectance-boosting coating and silver-overcoat on aluminum where the high-index material was antimony trioxide and the low-index material was cryolite. The quartz crystal monitor consists of a thin slice of quartz with surface electrodes forming the resonator of an oscillator. The principle of this type of mass monitor is to expose the crystal to the evaporant stream and to measure the change in frequency as the film deposits and the mass increases. However, the mechanical vibrational modes of a slice of quartz crystal are very complicated. Thus the resonant frequency of the quartz crystal is not only dependent on the mass of the growing films, but also on their mechanical properties, such as density and shear modulus. So the monitoring of different materials, especially for multilayer coatings, on

the same crystal would cause significant errors if the system were not recalibrated before depositing another material.

There are several ways to describe the relationship between the thickness of the growing film and the resonance frequency of the crystal. The thickness frequency equation used for the manufacture of the candidate coatings is given by

$$T_f = -\left(\frac{N_q D_q}{D_f F_q}\right) (F_c - F_q) \quad (4.2)$$

where

T_f = film thickness (cm)

D_q = density of quartz ($\frac{\text{gm}}{\text{cm}^3}$)

D_f = density of film ($\frac{\text{gm}}{\text{cm}^3}$)

$N_q = F_q L_q$ = frequency constant for AT-cut quartz crystal (Hz-cm)

L_q = thickness of quartz crystal (cm)

F_q = resonant frequency of unplated crystal (Hz)

F_c = resonant frequency of loaded crystal (Hz).

A more accurate relationship between film thickness and resonant frequency was discussed by Miller and Bolef (1968) . They treated the quartz-film composite as a one dimensional compound acoustical resonator. Their results indicated that the elastic properties of the deposited film should be related to the frequency shift. Further study

of their original solution resulted in a simpler thickness frequency equation in the form of

$$T_f = \left(\frac{N_q D_q}{\pi D_f F_c Z} \right) \text{TAN}^{-1} \left(Z \text{TAN} \left(\pi \frac{F_q - F_c}{F_q} \right) \right) \quad (4.3)$$

where

$$Z = \left(\frac{D_q \mu_q}{D_f \mu_f} \right)^{1/2}$$

is the acoustic impedance ratio with μ_f and μ_q the shear moduli of deposited film and quartz crystal, respectively. The above equations were extracted from the instruction manual for thin film deposition controllers XMS-1 and XMS-3, Inficon Leybold-Heraeus Inc.

Since the density and the shear moduli of the deposited film are involved in the thickness-frequency equation, it is always difficult to monitor a multilayer coating without knowing the mechanical properties of the deposited film. In addition, we have to assume a constant index for the deposited film so that we can calculate the geometrical thickness (by dividing optical thickness by refractive index). We then monitor the geometric thickness, in terms of the resonant frequency of the crystal, for each layer. However, although the mass-monitoring method may be oversimplified, the candidate coatings with high-index layer, antimony trioxide and low-index layer, cryolite, were manufactured quite satisfactorily using this technique.

For the coatings where the high-index material is tantalum pentoxide and the low-index silicon dioxide, optical monitoring was considered to be a better technique, because the indices of these oxide materials are more sensitive to environmental parameters such as temperature, vacuum pressure, and evaporation rate. For example, the refractive index of tantalum pentoxide varies from 2.01 to 2.23(at $\lambda=550$ nm) as reported by Rubio (1982), Khawaja (1975), Westwood (1974), and Demiryont (1985). It was therefore considered better to monitoring the optical thickness directly, instead of the geometrical thickness.

For most effective application of optical monitoring in the construction of the candidate coatings, we should monitor the optical thickness in the ultraviolet region since the design is based on quarterwave thicknesses at wavelength 300 nm. Unfortunately, the necessary ultraviolet light source and detector were not available in the coating plant (BA 510) and so it was impossible to use direct monitoring, where the measurements for the control of layer thickness are made on the actual component which is to be produced. Indirect monitoring, where the measurements are made on a series of separate test plates, which in our case would be monitored in the visible region, was therefore the most appropriate technique. Since a monitor wavelength in the visible region is greater than the reference wavelength of the original design, the quarterwave thickness based on the reference wavelength of 300 nm must be decreased by the ratio of the actual monitoring wavelength and 300 nm in order to achieve the desired optical performance. However, the total variation of the

transmission of the test plates, due to the growing film, is also reduced by monitoring in the visible region, which makes the coating more difficult to achieve. For this reason some pre-coated test plates consisting of quarterwaves of zinc sulphide were used to enlarge the variation of the transmitted signal, especially when the low-index material was deposited.

The level of transmittance or reflectance from an optical monitor is certainly the most important information for a plant operator who must close the shutter at the proper time. But optical thickness control in terms of the transmittance or reflectance of a monitor plate is never absolutely accurate. So it is useful theoretically to calculate the thickness tolerance and signal errors before attempting manufacture. Now, let us suppose the thickness tolerance is less than 10 % (see Chapter 3, tolerance requirement for the candidate coatings), then how accurate should the signal from the monitor be? The relationship between thickness tolerance and signal error was derived by Macleod (1969) (on pp. 238-239). Here we follow his derivation and estimate the manufacturing tolerance of the candidate coatings. Suppose that in the monitoring of a single quarterwave layer there is an error, γ , in the value of reflectance at the termination point. This will give rise to a corresponding error ϕ in the phase thickness of the layer, δ , where

$$\delta = \left(\frac{\pi}{2}\right) - \phi . \quad (4.5)$$

Because of the nature of the characteristic reflectance curve of the

signal layer, the error in phase thickness will be rather greater in proportion than the original error in reflectance. The admittance of the layer will be given by the characteristic matrix:

$$\begin{bmatrix} \cos \delta & i \sin \delta / \eta \\ i \eta \sin \delta & \cos \delta \end{bmatrix} \begin{bmatrix} 1 \\ N \end{bmatrix} \quad (4.6)$$

where

$\cos \delta = \sin \phi$, $\sin \delta = \cos \phi$, η is the refractive index of the deposited film, and N is the refractive index of the substrate. This gives

$$Y = \frac{\sin \phi + \frac{i(N \cos \phi)}{\eta}}{i \eta \cos \phi + N \sin \phi} \quad (4.7)$$

Introducing the approximations for $\sin \phi$ and $\cos \phi$ up to and including powers of the second order, we have

$$Y = \frac{\phi + i\left(\frac{N}{\eta}\right)\left(1 - \frac{\phi^2}{2}\right)}{i \eta \left(1 - \frac{\phi^2}{2}\right)} \quad (4.8)$$

and the reflectance of the monitor in vacuum will be given by

$$R = \left(\frac{(N-1)\phi + i\left(\eta - \frac{N}{\eta}\right)\left(1 - \frac{\phi^2}{2}\right)}{(N+1)\phi - i\left(\eta + \frac{N}{\eta}\right)\left(1 - \frac{\phi^2}{2}\right)} \right)^2 \quad (4.9)$$

$$R = \left(\frac{(N-1)\phi + i(\eta - \frac{N}{\eta})(1 - \frac{\phi^2}{2})}{(N+1)\phi - i(\eta + \frac{N}{\eta})(1 - \frac{\phi^2}{2})} \right)^2 \quad (4.9)$$

which simplifies to

$$R = \frac{(\eta - \frac{N}{\eta})^2}{(\eta + \frac{N}{\eta})^2} \left(1 + \frac{4N(N^2+1-\eta^2-\frac{N^2}{\eta^2})\phi^2}{\eta^2-\frac{N^2}{\eta^2}} \right) \quad (4.10)$$

The values of γ and ϕ are related as follows

$$\gamma = \frac{4N(N^2+1-\eta^2-\frac{N^2}{\eta^2})}{(\eta^2-\frac{N^2}{\eta^2})^2} \phi^2 = \sigma \phi^2 \quad (4.11)$$

since the first factor in (4.10) is just the reflectance when γ and ϕ are both zero. Similarly, the transmittance of the monitor in vacuum is

$$T = 1-R = \left(1 - \frac{(\eta - \frac{N}{\eta})^2}{(\eta + \frac{N}{\eta})^2} \right) \left(1 + \frac{(\eta - \frac{N}{\eta})^2}{4N^2} \frac{4N(N^2+1-\eta^2-\frac{N^2}{\eta^2})\phi^2}{(\eta^2-\frac{N^2}{\eta^2})^2} \right) \quad (4.12)$$

assuming no absorption in the deposited film. Now the errors in transmittance of the monitor and in the phase thickness are related as follows

$$\gamma' = \frac{(\eta - \frac{N}{\eta})^2}{4N^2} \frac{4N(N^2 + 1 - \eta^2 - \frac{N^2}{\eta^2})\phi^2}{(\eta^2 - \frac{N^2}{\eta^2})^2} = \sigma'\phi^2 \quad (4.13)$$

again the first factor is just the transmittance when γ' and ϕ are both zero. Assume we want to monitor a $\frac{1}{8}$ th wave of Ta_2O_5 on a glass substrate where $\eta=2.136$ and $N=1.516$ at 600 nm and the maximum thickness error is 10 %, then the phase thickness error (ϕ) in terms of $\frac{1}{8}$ th wave is 10% x (phase thickness of $\frac{1}{8}$ th wave) = $0.01 \times \frac{\pi}{4}$. Therefore the maximum acceptable error from the monitor is $\gamma' = \sigma'\phi^2 \approx 0.3$ % (equation 4.13) which is around the limit of the electronics. Shortening the monitoring wavelength can increase the tolerance in γ' , so that the coating will be easier to achieve.

However, the monitoring wavelength of the candidate coatings that we have made was in the visible region. According to the equations derived above, the coatings should be more difficult to make with visible than with ultraviolet monitoring. Numbers of test runs for the manufacture of the candidate coatings have proved this point.

Once the monitoring wavelength is chosen, we can calculate the transmission of the monitoring plate that is going to receive the same amount of material as the substrate. This gives the value of the transmission which we should read from the monitoring system at the terminal point of each layer. The working procedure is as follows: 1. Use the calculated values of the transmittance of the monitoring plate for each layer to make a test run separately. 2. Measure the actual

thickness of the film on the substrate by using a profilometer. 3. Calculate the tooling factor which is the ratio of the actual optical thickness on the substrate and the optical thickness on the monitoring plate. 4. Use the tooling factor to correct the calculated value of the transmission of the monitoring plate, the result is the improved terminal point for the next run. 5. Repeat until good optical performance of the candidate coatings is obtained.

The tooling factor here is mainly dependent on the geometrical arrangement of the substrate and the monitoring plate, and on the vapor distribution of the source. It is different for each coating plant. For the BA510 coating plant (see the geometrical setup of the BA510 in Figure 4.9), we eventually derived the following values for the transmittance of the monitoring plate in the deposition of the reflectance-boosting silver coating as: 1. Transmittance starts at 92 % and ends at 88 % for the tantalum pentoxide layer. 2. Transmittance starts at 66.5 % and ends at 73 % for the silicon dioxide layer, where a quarterwave zinc sulphide pre-coated monitoring plate is used. 3. Transmittance starts at 66.5 % and ends at 72 % for the aluminum oxide layer, again using a similar pre-coated monitoring plate. The monitoring wavelength for the coating is 600 nm and other conditions are : evaporation rate for each dielectric layer less than 2 Å per second, substrate at room temperature, and pressure of 10^{-6} torr. Following the above procedure, the candidate coatings were manufactured quite satisfactorily.

Fig. 4.9 The geometrical setup of the coating plant BA510.

CHAPTER 5

ENVIRONMENTAL TESTING

The greatest problem in connection with the coatings is their service life. In this connection, we were informed by L. D. Barr, Kitt Peak National Observatory that the sapphire-overcoat silver on the 1.2 m infrared telescope deteriorated within ten months to the point where it had to be replaced. So it is useful to compare the durability of the candidate coatings with that of the plain aluminum, silver, and sapphire over silver coatings in laboratory testing. Such results assist us to estimate the life of the candidate coatings before completion of long-term testing.

The improved durability of the copper-based coating will be discussed in the next section, but the analysis and the model for this improved durability improved coating will be left until Chapter 6. The surface plasmon behaviour deduced from the optical performance of the reflectance boosting coating will be discussed in the last section of this chapter. In this section, we will also explain the effects of the reduction of the surface plasmon in step with the decreasing of the electric field across the interface between the silver and sapphire layer. The theory is based on that in Chapter 2.

Durability of the Candidate Coatings

Probably the most severe environmental agent which the coating will have to face is humidity. Since the columnar structure intrinsically exists for any thin film deposited by thermal evaporation, atmospheric moisture can always penetrate the coating and condense within the voids or even accumulate between the coating and the substrate. The water can chemically react with the coating to change the optical properties, or rupture the chemical bounds between coating and substrate, causing an adhesion failure.

One technique for verifying environmental stability is to expose test samples to high humidity. A Blue M Vapor-Temp environmental chamber (see Figure 5.1) was set at 40°C and 94 % relative humidity for a test series. All coatings were deposited on 2 inch square microsheet glass substrates and were inserted into the high humidity chamber simultaneously. A single sample-holder accommodates all the samples together with a proper space in between adjacent ones. Samples of aluminum, and silver overcoated with sapphire a quarterwave thick at 600 nm, were included as controls. As expected, the aluminum lasted longest; holes appeared in this coating after 10 to 14 days exposure. The sapphire overcoated silver was badly damaged after only 20 hours exposure (Figure 5.2 (a) and (b)). The candidate coatings resisted slightly better, but after 48 hours, they developed moisture patches and quickly deteriorated thereafter (Figure 5.2 (c), (d), (e), and (f)). While the four-layer boosting overcoat was clearly an improvement over the single sapphire layer, a linear extrapolation implied a lifetime of

Fig. 5.1 Sideview of the humidity chamber.

(a)

(b)

Fig. 5.2 Photographs of the surfaces of coatings after varying degrees of exposure to 94% relative humidity at 40°C.

(a) Front and (b) rear surface after 20 hours' exposure of a coating of design: Air|Al₂O₃|Ag|Glass.

(c)

(d)

Fig. 5.2 (c) Front and (d) rear surfaces after 2 days' exposure of a coating of design (KP-105-1): Air|Ta₂O₅|SiO₂|Ta₂O₅|Al₂O₃|Ag|Glass.

(e)

(f)

Fig. 5.2 (e) Front and (f) rear surfaces after 2 days' exposure of a coating of design (KP-105-3): $\text{Air}|\text{Ta}_2\text{O}_5|\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{Al}_2\text{O}_3|\text{Ag}|\text{Glass}$.

perhaps two years rather than 10 months, which was still considered inadequate. The coating consisting of silver-overcoated aluminum is not shown in Figure 5.2. It was given up in the early stages because of the instability of the thin silver layer which meant that the coating could not compete with the reflectance boosting coating.

Improved Durability of the Copper-based Coating

The requirement that the coatings be deposited at ambient rather than elevated temperatures is a major handicap, which enhances the porosity of the dielectric overcoat and reduces its protective function. Changing materials in the overcoat seems unlikely to improve matters. Ion-assisted deposition to densify and toughen the dielectric layers is one possible solution, which was described by Martin, Macleod, Netterfield, Pacey, and Sainty (1983), but this has not been applied on the scale required for large telescope mirrors. So, an alternative solution was sought in which the resistance of the silver itself might be improved. Some form of cathodic protection based on copper was considered; copper's position in the electrochemical series and its strong adherence to silver (Keller, 1963) suggested it could help in this regard. A number of experiments were performed in which potentials were applied to coatings containing the two metal films, none of which were successful. Portions of the coating showed less damage while other parts showed enhanced corrosion. However, it was observed that copper-silver coatings with no applied potential, which were included as controls, showed greatly improved durability. It is worth noting that thick overlayers of electroplated copper have long been used as

protection for second surface chemically deposited silver mirrors.

To take advantage of this effect, a copper underlayer was inserted in the coating design based on the thick silver layer with a boosting dielectric overcoat. The coating was then subjected to testing in the environmental chamber. Samples withstood 7 to 14 days' exposure to an atmosphere of greater than 94 % relative humidity at a temperature of 40 °C before faint spots appeared, putting them at the same durability level as aluminum. A typical result is shown in Figure 5.2 (g) and (h).

Silver is also prone to attack by atmospheric sulfur compounds, so we also assessed the resistance of the copper-silver combination to attack by such agents. We tested this sensitivity by exposing the coatings for five minutes to the atmosphere above a solution of 2 ml of 22 % $(\text{NH}_4)_2\text{S}$ solution in 18 ml of water. For this test, the dielectric layers above silver were omitted so that the corrosion resistance of the silver was measured directly. It was quite clear even to the naked eye that the silver deposited over copper was superior to the plain silver. This is confirmed by reflectance measurements after the corrosion test, some of which are reproduced in Figure 5.3. The complete coating based on a thick silver layer with boosting dielectric layers and copper underlayer was also investigated under the same conditions; the measurements show no significant change of coating reflectance after one hour in the testing chamber. We may conclude that the durability of the silver-copper coating has been greatly improved by the copper underlayer, and note the promise of the reflectance-boosting silver

(g)

(h)

Fig. 5.2 (g) Front and (h) rear surfaces after 7 days' exposure of a copper-based coating of design: $\text{Air}|\text{Ta}_2\text{O}_5|\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{Al}_2\text{O}_3|\text{Ag}|\text{Cu}|\text{Glass}$.

Fig. 5.3 Measured reflectance of coating after five minutes' exposure to the atmosphere above a solution of 2ml 22% $(\text{NH}_4)_2\text{S}$ in 18ml water. The silver in each case was 100nm thick and the copper 40nm thick.

coating for use on telescope mirrors.

Surface Plasmon of the Silver-based Coating

The performance of this copper-based coating is shown in Figure 5.4 together with the theoretical characteristics. The principal difference between the curves is a slightly reduction in the observed reflectance with respect to the theoretical at shorter wavelengths. The slight dip around 380 nm is due to a surface plasmon of silver, noted by Stanford and Bennett (1969), and Jaspersen and Schnatterly (1969). They showed that only the surface roughness of the silver foil was found to contribute significantly to the intensity of the surface plasmon. Sapphire-overcoated silver was a typical case they investigated. Increasing the roughness of the sapphire surface also enhanced the surface plasmon.

However, in their reports, only a single layer of sapphire was deposited over the silver so that the electric field distribution was constant across the interface of silver and sapphire. Additional deposited layers over the sapphire silver can change the electric field distribution inside the coating, and therefore affect the intensity of the surface plasmon.

The electric field can be calculated by the following equation (see equation 2.37)

$$E = \frac{\text{Constant}}{\text{square root of admittance}} \quad (5.1)$$

Fig. 5.4 Measured and calculated performance of the boosted silver coating with copper underlayer.

In this way the electric field in the four-layer boosting coating can be plotted as a function of depth within the coating as shown in Figure 5.5. The most interesting feature that was found was that the electric field across the interface of the silver and the sapphire layer (see Figure 5.5 (a)) decreased by a factor of two after an additional tantalum pentoxide layer was deposited (see Figure 5.5 (b)). This effect predicted that the surface plasmon would be reduced if the additional layer was thin enough to avoid introducing too much additional surface roughness. The optical performance of the two-layer boosting coating proved this prediction as shown in Figure 5.6. Adding yet another low-index layer over the two-layer boosting coating will slightly increase the electric field across the silver surface (see Figure 5.5 (c)), but the surface plasmon stays almost at the same intensity showing that the surface roughness remains at the same level as before. Increasing still further the number of dielectric layers will increase the surface roughness and this may enhance the surface plasmon even although the electric field may be decreased, by, for example adding a high-index layer.

However, the electric field of the four-layer boosting coating (see Figure 5.5 (d)) at this sapphire-silver interface is never greater than that of simple sapphire overcoated silver. A well-polished mirror coated by the reflectance boosting layers should not generate as intense a surface plasmon as found by Stanford and Bennett. The optical performance of the four-layer boosting coating, which was deposited on two-inch glass slides showed about 5 % reduction of reflectance around 380 nm wavelength in Figure 5.4. This implies the reduction of the

ELECTRIC FIELD IN VOLT/METER

E-FIELD DISTRIBUTION OF AL₂O₃/AG

Fig. 5.5(a) Electrical field distribution inside a coating of design: Air|0.8Al₂O₃|Ag, with reference wavelength 300nm but calculated at 380nm.

ELECTRIC FIELD IN VOLT/METER

E-FIELD DISTRIBUTION OF TA2O5/AL2O3/AG

Fig. 5.5(b) Electrical field distribution inside a coating of design: Air|Ta₂O₅|0.8Al₂O₃|Ag, with reference wavelength 300nm but calculated at 380nm.

ELECTRIC FIELD IN VOLT/METER

E-FIELD DIS. OF SiO₂/TA₂O₅/AL₂O₃/AG

Fig. 5.5(c) Electrical field distribution inside a coating of design:
Air|SiO₂|Ta₂O₅|0.8Al₂O₃|Ag, with reference wavelength 300nm but
calculated at 380nm.

ELECTRIC FIELD IN VOLT/METER

E-FIELD DIS. OF TA2O5/SIO2/TA2O5/AL2O3/AG

Fig. 5.5(d) Electrical field distribution inside a coating of design: Air|Ta₂O₅|SiO₂|Ta₂O₅|0.8Al₂O₃|Ag, with reference wavelength 300nm but calculated at 380nm.

Fig. 5.6 Measured performances of the boosted silver coating with copper underlayer. (a) with a single Al_2O_3 layer, (b) with $(\text{Ta}_2\text{O}_5|\text{0.8Al}_2\text{O}_3)$ two layers, (c) with $(\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{0.8Al}_2\text{O}_3)$ three layers, and (d) with $(\text{Ta}_2\text{O}_5|\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{0.8Al}_2\text{O}_3)$ four layers.

reflectance caused by the surface plasmon should be less than 5 % if the four-layer boosting coating is deposited on a well polished mirror, which is invariably the case for all telescope mirrors.

CHAPTER 6

ANALYSIS

In this chapter we will describe several different techniques that we have used to analyze the copper-based coating which has shown greatly improved durability compared with the coating without the copper underlayer. Copper may physically change the structure of the silver film and/or chemically react with environmental agents, thus inhibiting the corrosion of the silver. However, it would not be acceptable if the copper underlayer were to degrade the optical performance of the silver-based coating in improving its durability.

The reflectance of an unprotected silver layer deposited over copper is shown in Figure 6.1 together with theoretical values extracted from Hass and Hadley (1972). The measured curve is marginally lower than the theoretical in the 350 nm to 400 nm region. This discrepancy is small and could simply represent errors in measurement. So we may conclude that the copper underlayer has no significant effect on the reflectance of the front face of the overlying silver layer.

Rate of Corrosion in Sulfur

The variation of reflectance with time in the sulfur corrosion test was also explored. Four different coatings, plain silver, silver deposited over copper, silver deposited over gold, and silver deposited over chromium, were put into the chamber as shown in Figure 6.2. A

Fig. 6.1 Measured reflectance of 100nm silver with underlayer of 40nm copper. The points are theoretical figures from Hass and Hadley.

Fig. 6.2 Schematic diagram of experimental setup for the rate corrosion measurement.

bottle contained a solution of 2 ml of 22 % $(\text{NH}_4)_2\text{S}$ solution in 18 ml of water was attached to the base of the chamber, and then generated a proper dense sulfur-atmosphere in the chamber. Monochromatic incident light was derived from a tungsten lamp and a monochromator, passed through a beamsplitter, and then reflected from the sample back to a silicon detector. The signal was synchronized with a chopper and lockin amplifier, and then recorded by a chart recorder. Since only one sample could be measured at a time, careful calibration of the initial point and replacement of the sulfur-solution were carried out immediately before each measurement.

Typical measurements are reproduced in Figure 6.3. To emphasize the significant part near the start of the curves, a magnified portion of this region is replotted in Figure 6.4. All curves, with the exception of the silver over copper specimen, show a rapid fall in reflectance of approximately the same slope. The silver on copper, however, remains almost constant for a time before falling at essentially the same rate as the others. Corrosion is clearly being inhibited for a period, perhaps by a material that is eventually exhausted.

Grain Size Electron Microscopy

It is interesting to look at the microstructure of the silver film with copper underlayer compared with that of the plain silver film. Shadowed direct replicas of plain silver and silver on copper were prepared for transmission electron microscopy. Samples of the silver-copper coating and silver only coating were made in the BA 510 coating plant, and then the correct thickness of platinum and carbon films were

Fig. 6.3 Reflectance with respect to time for four different film designs exposed to the ammonium sulfide solution described in the text.

Fig. 6.4 Reflectance with respect to time for the four different films of figure 6.3 with an expanded time scale to show the constant reflectance region for film with the copper underlayer.

deposited over the cross section and surface of the coatings in a two-inch coating plant dedicated to this operation. A solution of 5 ml of HF solution in 95 ml of water was used to etch away the coating and leave the carbon replicas with platinum shadowing floating on the surface. Then, we used the standard small circular copper grids, which are the replica holders for transmission electron microscopy, carefully to fish out the carbon replicas. When dry, the samples were ready for insertion in the microscope.

The results are shown in Figure 6.5. In each case, the silver layer was 100 nm thick and the copper underlayer was 40 nm. The magnification for both samples was set at 4800. When deposited over copper, the grain structure of silver is apparently finer by roughly an order of magnitude. This shows that the physical structure of the silver film has been changed by the copper underlayer.

Optical Microscopy of Grain Size after Corrosion

Three different coatings, silver deposited over gold, silver deposited over copper, and plain silver were simultaneously exposed to the dense sulfur-atmosphere, which was generated by a solution of 2 ml of 22 % $(\text{NH}_4)_2\text{S}$ solution in 18 ml of water. After five minutes, coatings were moved out the chamber and photographed in an optical microscope.

Figure 6.6 show an enlargement of the black spots in the coating resulting from sulfur corrosion. Figure 6.6 (a) and (b), and Figure 6.6 (c) and (d) represent plain silver and silver deposited over gold. They all show a very fine grain size of the corrosion. However the silver deposited over copper shows rather coarser grains in the corroded area

Fig. 6.5 Transmission electron micrographs of shadowed replicas of (a) a 100nm silver film on glass and (b) a 100nm silver film over a 40nm copper film.

Fig. 6.6 The corroded plain silver coating taken in an optical microscope (a) in reflection mode, (b) in transmission mode. The coatings were exposed to the ammonium sulfide solution described in the text.

Fig. 6.6 (c) The corroded silver over gold coating taken in an optical microscope in reflection mode, (d) in transmission mode.

Fig. 6.6 (e) The corroded silver over copper coating taken in an optical microscope in reflection mode, (f) in transmission mode.

than the other two coatings (see Figure 6.6 (e) and (f)) and a larger uncorroded area is present on the silver surface. This tends to indicate that the copper underlayer has changed the corrosion mechanism of the silver film.

Copper and Aluminum Overcoats on Silver

It is possible that at least some of the improvement in durability is chemical in origin, and an experiment was devised in which grain sizes were identical. A thick silver layer was deposited directly onto a glass substrate and then was overcoated at one end with aluminum and at the other with copper leaving an exposed strip of silver in between. The edges of the copper and aluminum films were intentionally made as sharp as possible. A movable shutter which is near the substrate inside the coating plant can cover part of the sample and expose the other part for depositing aluminum, and then move back to leave some silver coated area for depositing copper. The thickness of the aluminum layer was 40 nm and the copper layer 35 nm. Several samples were then subjected to the sulfur corrosion test. The silver and copper films were badly tarnished, while the aluminum film was not visibly affected. However, beside the edge of the copper overlayer was a 0.7 mm wide untarnished strip of silver. A similar strip beside the aluminum edge was so narrow that it could only be seen by the naked eye with difficulty. Microscopic measurements showed it to be approximately $\frac{1}{7}$ th of the width of the strip beside the copper (Figure 6.7). This demonstrates that the corrosion inhibition occurs independently of grain

a

b

Fig. 6.7 Results of a corrosion test in which a 100nm silver film with copper and aluminum overlayers on opposite edges was subjected to atmospheric exposure above a solution of 2ml 22% $(\text{NH}_4)_2\text{S}$ in 18ml water. (a) shows the appearance of the strip of silver next to the edge of the aluminum and (b) shows that of the silver next to the copper. The strip of uncorroded material in (b) is approximately 0.7mm wide, or seven times that in (a).

size.

Rutherford Backscattering Results

Rutherford Backscattering (RBS) was used to study the variation of composition with depth of the silver over copper coatings. In this technique, particles, usually singly-ionized, of energy in the range of 2 Mev, are energized by a Van de Graaff accelerator, and then bombard the sample which is placed in vacuum. The energy of reflected α particles is a function of the atomic number and the depth of the scattering atom. The energy distribution of the backscattered α particles therefore gives information on the variation of composition with depth of a coating.

The results of RBS scans of silver and copper layers are shown in Figure 6.8. The small peak in between the large copper peak and the silver peak is surface copper. That it is surface copper was verified by tilting the samples with respect to the ion beam; the small peak remained in exactly the same position, indicating its location at the surface of the silver film. There is no evidence of copper in the interior of the silver, but only at the surface. This is also evidence that the copper is indeed over the silver and not the result of a pinhole. This is additional evidence that the improved durability of the silver-copper coating is due to surface copper.

Model for the Durability Improvement

The electron microscopy has shown that the grain size of the silver with copper underlayer is finer than that of the plain silver coating. According to solid state physics, the grain size of the crystal

Fig. 6.8 Rutherford backscattering data showing the number of backscattered helium nuclei as a function of ion energy, which is proportional to the mass of the scattering nuclei in the film material. The highest atomic mass is that of silver, which appears as the peak on the right. The small concentration of copper on the film surface appears next as a very small peak, followed by the larger peak for the copper underlayer itself. The energies of the latter are reduced by passage of the ions through the overlying silver layer. Lower mass elements in the substrate appear on the left side of the curve.

is related to corrosion speed. The finer the grain size the faster the corrosion because there is a greater fraction of grain boundary material to be attacked by environmental agents. Consideration only of grain size should indicate a corrosion rate of the coating with the copper underlayer greater than the coating without copper. This is clearly the opposite of the experimental results which show the copper underlayer greatly improving the durability of the silver-based coatings. So we may conclude that the physical change in the structure of the silver film should not be the main reason for the improved durability. Chemical effects therefore become more important.

The Rutherford Backscattering results show that a small amount of copper has appeared on the surface of the silver film. The copper may appear on the surface due to diffusion after deposition, or it may be included in the silver film during its growth. Clearly, from the corrosion experiments it reacts chemically with the agents and successfully inhibits the corrosion of the silver until it is eventually exhausted. This has been demonstrated by the experiments on corrosion rate. Whether or not this model is correct, copper has certainly a very beneficial effect on the silver coating.

CHAPTER 7

FIELD TEST

Although the improved durability of the coating was demonstrated by the high humidity and sulfur tests in the laboratory, the lifetime of the coating under actual operating conditions had to be determined as well. Samples of the coating, based on thick silver with a copper underlayer and boosting dielectric overlayers, together with a similar coating without the copper layer, and a coating of sapphire over silver, have been placed on the four-meter telescope at Kitt Peak National Observatory. The samples were put into a slide which exposed the coated surfaces to the atmosphere (see Figure 7.1). Since they were actually mounted on the metal stop at the periphery of the primary mirror, they were subjected to essentially the same environment as the primary.

During the exposure, water vapor and sulfur compounds in atmosphere will attack the coatings, causing deterioration. One method of comparison of the durability of the coatings is to measure the reflectance of the samples before and after a period of time. Figure 7.2 (a), (b), and (c) show the reflectance of the samples measured immediately after manufacture and then after one year of exposure on the mountain, that is, 16 months after manufacture. As one would expect, the sapphire overcoated silver was damaged much more than the others. The measured reflectance of the sapphire overcoated silver is about 10 to 20 % lower than before. The drop in reflectance for the

Fig. 7.1 Picture of the sample holder which was mounted on 4-meter telescope.

Fig. 7.2(a) Reflectance for coating of design: Air|Al₂O₃|Ag|Glass, exposed for one year on Kitt Peak. Solid and dashed lines show reflectance before and after the test.

Fig. 7.2(b) Reflectance for coating of design:
 Air|Ta₂O₅|SiO₂|Ta₂O₅|Al₂O₃|Ag|Glass, exposed for one year on Kitt Peak.
 Solid and dashed lines show reflectance before and after the test.

Fig. 7.2(c) reflectance for coating of design:
 Air|Ta₂O₅|SiO₂|Ta₂O₅|Al₂O₃|Ag|Cu|Glass, exposed for one year on Kitt Peak.
 Solid and dashed lines show reflectance before and after the test.

other coatings was less than 3 %. However, the coatings were not cleaned before the measurement in order to avoid further damage and so that this test could continue, so some of the reflectance reduction was due to the scattering loss from the dust on the coating surface. The difference of the reflectance between the candidate coating without copper and with copper is not significant. This implies the life for both coatings of longer than one year at least.

Pictures showing the physical damage appear in Figure 7.3 (a), (b), and (c). Since the coatings were not cleaned before taking the photos, the dust is clearly visible in the photographs. Nonetheless, the improved performance of the copper-based coating is evident.

Fig. 7.3 Photographs of films after exposure for one year on Kitt Peak: (a) coating of design: $\text{Air}|\text{Al}_2\text{O}_3|\text{Ag}|\text{Glass}$; (b) coating of design: $\text{Air}|\text{Ta}_2\text{O}_5|\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{Al}_2\text{O}_3|\text{Ag}|\text{Glass}$; (c) coating of design: $\text{Air}|\text{Ta}_2\text{O}_5|\text{SiO}_2|\text{Ta}_2\text{O}_5|\text{Al}_2\text{O}_3|\text{Ag}|\text{Cu}|\text{Glass}$.

CHAPTER 8

CONCLUSION

We now conclude with a brief summary of the results of the study of the silver-based coating for telescope mirrors, followed by some suggestions for future work.

Summary

In Chapter 3, we proposed two silver-based coating designs for telescope mirrors which required high reflectance from the near ultraviolet through the infrared. These proposed coatings provide increased reflectance and lower emissivity for infrared astronomical observations, but additionally have 98 % reflectance in the visible region and above 65 % reflectance in the near ultraviolet.

To avoid difficulties in the early manufacture, the candidate coatings were first attempted with well known materials. Sapphire was used for the diffusion barrier layer as well as the best overcoat. Antimony trioxide and cryolite were used as high and low index layer for the coatings. These candidate coatings were manufactured quite satisfactorily, and the measured reflectance was close to the theoretical calculation.

In Chapter 4, we discussed the requirements of thickness tolerances and uniformity, followed by the monitoring methods for the manufacture of the coatings. The calculations of manufacturing

tolerances was based on Monte Carlo simulation of the manufacturing process where we assumed that the error in any one layer was completely independent of that in any other. The theoretical calculation showed that the optical performance of both the boosting coating and the silver overcoat were acceptable if the thickness error in any layer could be kept below 10 %. This should not present any difficulties in a well-maintained plant with standard monitoring facilities.

For the candidate coatings, we have considered the wavefront error due to the lack of uniformity in either the metal layer or the multilayer coatings. The calculation was based on the thickness change for the coatings if the wavefront error is not to exceed $\frac{\lambda}{20}$ or $\frac{\lambda}{40}$. The wavefront error generated by changes in thickness may be compensated by the phase shifts in the multilayers. For this reason the silver overcoat appears superior even to a metal layer, while the boosting overcoat appears less critical than a metal layer over much of its range, but at longer wavelengths its uniformity requirement becomes more severe. This may imply that the candidate coatings should not present any uniformity problems greater than those for normal multilayers if the thickness error is less than 5 %.

The quartz crystal monitoring technique was first used to monitor the well known materials such as antimony trioxide and cryolite in the candidate coatings. For the tougher materials such as tantalum pentoxide and silicon dioxide, we used an optical monitoring method because of the greater risk of instability of these materials. However, although the theoretical calculations showed that to monitor the

thickness with an error of less than 10 % was difficult if the monitor wavelength was not in ultraviolet region or the same as the reference wavelength (300 nm) for the coating designs, the candidate coatings consisting of the tougher materials were manufactured satisfactorily.

The surface plasmon of silver, which may reduce reflectance by 5 % in the vicinity of 380 nm, was discussed in Chapter 5. Both the theoretical calculation and the experimental measurement showed that the effects of the surface plasmon would be decreased if more than one dielectric layer was involved in boosting the silver or if the surface roughness of the substrate was improved.

Since a coating for a telescope mirror requires not only good optical performance but also long life, we have to consider the durability of the candidate coatings. The high humidity test and the sulfur test were set up in the laboratory to estimate the lifetime of the coatings compared with sapphire-overcoated silver and aluminum. The results showed that the reflectance-boosting coating with a copper underlayer had greatly improved durability, which might even put the lifetime of this coating at the same level as aluminum.

The analysis in Chapter 6 showed that adding the copper underlayer would result in a small amount of copper over the silver layer. This surface copper did not alter the optical performance of the silver, but exhausted itself preferentially when the coating was attacked by the sulfur or water compounds. This is probably one of the main reasons that the durability of the silver-based coating was greatly improved.

In Chapter 7, the field test results demonstrated that the reflectance boosting coating with the copper underlayer could last 16 months at least, although the test is still in progress. This experiment gives further evidence that the durability of the coating has been improved.

Suggestions for Further Work

The durability of silver coatings has been increased by adding a copper underlayer and reflectance-boosting dielectric overlayers. The lifetime of this coating is believed to be comparable with aluminum, although measurements are still in progress. These results were reported by Song, Sprague, Macleod, and Jacobson (1985). However, the problem of uniformity of dielectric overcoat deposited on large scale telescope mirrors must be solved if such silver coatings are to be adopted.

We now propose a method for approaching the uniformity requirement for large scale substrates. In 1974, J. V. Ramsay, R. P. Netterfield and E. G. V. Mugridge produced uniform thick films over large areas with uniformity errors of less than 0.1 % over substrates of diameter 200 mm. The technique uses a rotating substrate and a rotating mask situated between the source and the substrate, the axis of rotation of the mask being offset from the line joining the centre of rotation of the substrate and the centre of the source. However, conditions have to be changed before this technique may be applied to the coating of large scale telescope mirrors. First of all, the sources must be scaled up so that sufficient evaporated material can reach the large substrate.

Secondly, telescope mirrors are massive and yet precisely dimensioned so that it is difficult and undesirable that they should be rotated. It would therefore be an advantage if the sources could be rotated rather than the substrate. This would be equivalent, physically, to a rotating substrate. Finally, the correction mask should be close to the sources, so that although reasonable large, it should not increase the diameter of the coating chamber. Although theoretical calculation shows that an approach to the uniformity requirement of a large substrate is possible, more calculations and experiments must be performed before the manufacture can be assumed.

The life of the candidate coating can also be improved by using the technique of ion-assisted deposition instead of conventional deposition. Some optical materials such as tantalum pentoxide, silicon dioxide, and aluminum oxide have been studied by S. Saxe (dissertation 1985) and he has shown that the films could be densified if ions with correct energy were directed at the substrate during the film growth. It might be possible to generate energetic ions in the chamber which would bombard the source vapor rather than the large substrate. The vapor might gain more energy from the argon or oxygen ions so that their mobility on substrate might be increased. The effect of increased mobility is usually to densify films so that they exhibit increased resistance to moisture or other chemical agents which might attack the inner layers of the coating. This could improve the life of the candidate coating still further to the extent that silver-based coatings could become even more durable than aluminum as a coating for the

mirrors of large optical telescopes.

LIST OF REFERENCES

- Barr, L. D., Personal Communication, Kitt Peak National Observatory.
- Browning, S. D., Jacobson, M. R., Macleod, H. A., Potoff, R. H., Song, D. Y., and Van Milligen F., "Development of High Reflectance Coatings for Ground-based Astronomical Instruments," Proc. SPIE. 332, 310-314 (1982).
- Demiryont, H., Sites, J. R., and Geib, K., "Effects of Oxygen Content on the Optical Properties of Tantalum Oxide Films Deposited by Ion-beam Sputtering," Appl. Opt. 24, 490-495 (1985).
- Dubkov, V. M., and Rozhdestvenskii, V. N., "Protecting Reflecting Layers of Copper and Silver Against Tarnishing," Sov. J. Opt. Technol. 50, 35-36 (1983).
- Ferrell, R. A., "Angular Dependence of the Characteristic Energy Loss of Electrons Passing Through Metal Foils," Phys. Rev. 101, 554-563 (1956).
- Ferrell, R. A., "Predicted Radition of Plasma Oscillations in Metal Films," Phys. Rev. 111, 1214-1222 (1958).
- Guenther, K. H., "Columnar and Nodular Growth of Thin Films," Proc. SPIE 346, (1982).
- Hass, G., and Hadley, L., "Optical Constants of Metals," in American Institute of Physics Handbook, D. E. Gray, Ed., McGraw Hill, New York and London, 1972.
- Jasperson, S. N., and Schnatterly, S. E., "Photon-Surface-Plasmon Coupling in Thick Ag Foils," Phys. Rev. 188, 759-769 (1969).
- Keller, D. V., "Adhesion Between Solid Metals," Wear, 6, 353-365 (1963).
- Khawaja, E. E., and Tomlin, S. G., "The Optical Properties of Thin Films of Ta₂O₅ and ZrO₂," Thin Solid Films 30, 361-369 (1975).
- Lubezky, I., Ceren, E., and Klein, Z., "Silver Mirrors Protected with Yttria for the 0.5-14 μ m region," Appl. Opt. 19, 1895 (1980).
- Macleod, H. A., Thin-Film Optical Filters, Adam Hilger, London, 1969.
- Macleod, H. A., and Pelletier, E., "Error Compensation Mechanisms in Some

- Thin Film Monitoring Systems," *Optica Acta* 24, 907-930 (1977).
- Macleod, H. A., "Microstructure of Optical Thin Films," *Proc. SPIE* 325, 21-28 (1982).
- Martin, P. J., Macleod, H. A., Netterfield, R. P., Pacey, C. G., and Sainty, W. G., "Ion-beam-assisted Deposition of Thin Films," *Appl. Opt.* 22, 178-184 (1983).
- Miller, J. G., and Bolef, D. I., "Sensitivity Enhancement by the Use of Acoustic Resonators in CW Ultrasonic Spectroscopy," *J. Appl. Phys.* 39, 4589-4593 (1968).
- Motovilov, O. A., Lavrishev, A. P., and Smirnov, A. N., "Stable Narrow-band Interference Filters for the Visible Region," *Sov. J. Opt. Technol.* 41, 278-279 (1974).
- Ramsay, J. V., and Ciddor, P. E., "Apparent Shape of Broad Band Multilayer Reflecting Surfaces," *Appl. Opt.* 6, 2003-2004 (1967).
- Ramsay, J. V., Netterfield, R. P., and Mugridge, E. G. V., "Large-area Uniform Evaporation Thin Films," *Vacuum* 24, 337-340 (1974).
- Ritchie, R. H., "Plasma Losses by Fast Electrons in Thin Films," *Phys. Rev.* 106, 874-881 (1957).
- Ritchie, R. H., Arakawa, E. T., Cowan, J. J., and Hamm, E. T., "Surface-Plasmon Resonance Effect in Grating Diffraction," *Phys. Rev. Lett.* 21, 1530-1533 (1968).
- Rubio, F., Abella, J. M., Denis, J., and Martinez-duart, J. M., "Optical Properties of Reactively Sputtered Ta₂O₅ Films," *J. Vac. Sci. Technol.* 21, 1043-1045 (1982).
- Saxe, S., "Ion-induced Processes in Optical Coating," Ph.D. Dissertation, University of Arizona, 1985.
- Sommerfeld, A., "On the Broadening of Waves in Wireless Telegraphy," *Ann. Phys.* 28, 665-736 (1909).
- Song, D. Y., Sprague, R. W., Macleod, H. A., and Jacobson, M. R., "Progress in the Development of a Durable Silver-Based High-Reflectance Coating for Astronomical Telescopes," *Appl. Opt.* 24, 1164-1170 (1985).
- Song, D. Y., and Macleod, H. A., "Improved Coating for Large Astronomical Telescope Mirrors," To be published in *Proc. SPIE* (1985).
- Stanford, L. J., and Bennett, H. E., "Enhancement of Surface Plasma Resonance Absorption in Mirrors by Overcoating with Dielectrics,"

- Appl. Opt. 8, 2556-2557 (1969).
- Stern, E. A., and Ferrell, R. A., "Surface Plasma Oscillations of a Degenerate electron gas," Phys. Rev. 120, 130-136 (1960).
- Westwood, W. D., Boynton, R. J., and Ingre, S. J., "Effect of Pressure on the Properties of Reactively Sputtered Ta₂O₅," J. Vac. Sci. Technol. 11, 381-384 (1974).
- Wolf, W. L., and Zissis, G. J., Chapter 2 in The Infrared Handbook, 1978.
- Yves, J. C., "Surface Electromagnetic Waves," Ph.D. Dissertation, Cornell University, 1980.
- Zenneck, J., "Propagation of Plane Electromagnetic Waves Along a Plane Conducting Surface and its Bearing on the Theory of Transmission in Wireless Telegraphy," Ann. Phys. 23, 846-866 (1907).