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SOLVENT EVAPORATION TECHNIQUE
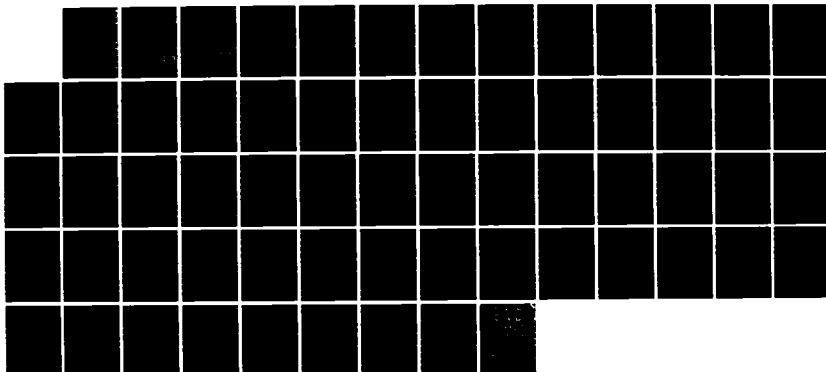FOR DEPOSITING THIN FILMS
ON OPTICAL SUBSTRATES

THESIS

Jeff L. Brown
Second Lieutenant, USAF

AFIT/GEP/ENP/85D-1

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DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

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SOLVENT EVAPORATION TECHNIQUE FOR DEPOSITING

THIN FILMS ON OPTICAL SUBSTRATES

THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering Physics

Jeff L. Brown, B.S.

Second Lieutenant, USAF

December 1985

Preface

Solvent evaporation has become a topic of renewed interest in recent years, especially in the area of optical interference coatings. As a research topic, it was desired to investigate the feasibility of producing interference coatings by such methods. In so doing, the chemical and physical nature of the topic was quite interesting, and I feel fortunate to have had the opportunity to take part in this research.

In reading this report, it is necessary to be familiar with the Fresnel equations and the basics of light interference. Chemical details have been kept to a minimum, and the reader should find the glossary helpful in defining unfamiliar terms.

I am indebted to many for their help in this research, some of which was crucial to my success in preparing an antireflection coating. From the Materials Lab, I wish to thank Dr. Robert Crane and the in-house research group of the Laser Hardened Materials Branch for the use of their equipment, and for their ideas and insights. Also, I am grateful for the time and patience of Mr. Neil McDevitt in teaching me how to use an ellipsometer, and for the generosity of Dr. Kent Eisentraut. From the Avionics Lab, I wish to thank Mr. Miller Meyer for his advice, and Dr. Kent Stowell for his support and encouragement.

I am also grateful for the help of Dr. Ernest Dorko and my faculty advisor Major John Wharton. Finally, I wish to thank my wife, who not only supported me through this endeavor, but who actually took part in the research and preparation of this report.

Jeff L. Brown

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Notation

n_0 = refractive index of surrounding medium

n_j = real part of refractive index of thin film layer j

k_j = imaginary part of refractive index of thin film layer j

n_s = real part of refractive index of substrate

k_s = imaginary part of refractive index of substrate

d_j = physical thickness of thin film layer j

R = reflectance (single interface)

T = transmittance (single interface)

λ_0 = reference wavelength

I_T = external transmittance

I_R = external reflectance

Δ, ψ = ellipsometer parameters

v = withdrawal velocity or pull rate

η = solution viscosity

ρ = solution density (wet film density)

g = acceleration of gravity

α, β = curve fitting parameters

Glossary

Alkoxide   Any substance containing an alkoxide group: RO-. An alkoxide ion RO^- is the conjugate base of an alcohol.

Colloid   Any substance in a state of fine subdivision or dispersion, with particles ranging between 10^{-5} and 10^{-7} cm in diameter.

Craze   To produce a network of fine cracks in a substance, especially a ceramic.

Gel   A rigid sol in which particles link together to form a structure with some strength.

Hydrolysis   Any reaction in which the water molecule is split and H and O atoms or OH groups from water are added to the products.

Peptization   The process whereby a coagulated colloid reverts to its original dispersed state.

Polymer   A large molecule made of many units of the same structure linked together.

Pyrolysis   Chemical decomposition by the action of heat.

Sol   A colloidal suspension of solid particles in a liquid.

Abstract

Interference coatings of titanium and zirconium oxide were prepared by a solvent evaporation, or sol-gel, process. Solutions of polymerized metal oxides were prepared from the hydrolysis reaction of diluted metal alkoxides. Coatings were applied to ordinary glass microscope slides by vertical withdrawal from the prepared solutions. Films with thicknesses of 25-200 nm were applied with excellent adherence and durability. Refractive indices and thicknesses were measured by ellipsometry. The transmission spectra of coated slides were measured and compared to theoretical calculations assuming no absorption. Quarter-wave layers of ZrO_2 on TiO_2 were produced as an antireflective coating at 465 nm.

SOLVENT EVAPORATION TECHNIQUE FOR DEPOSITING

THIN FILMS ON OPTICAL SUBSTRATES

I. Introduction

Thin film coatings on the surfaces of optical elements are of major

importance in the field of optics. Layers of such films, applied on

optical substrates, can produce advantageous interference effects. Thin

films can be applied as single layers or as multilayers, and can be pro-

duced using a variety of materials with a wide range of refractive in-

dices. The films thus produced can be used to modify the transmission

and reflection characteristics of ordinary optical substrates.

The most common method of depositing thin films on optical substrates

is vacuum deposition. This technique involves placing a substrate in a

high-vacuum chamber and evaporating a coating substance so that the evap-

orated substance fills the chamber. This is often accomplished by bom-

barding the coating substance with an electron beam. The evaporated

atoms are deposited onto the surface of the substrate where they con-

dense. Coatings made by this process can only be uniformly deposited on

one side of the substrate at a time.

A less widely used technique for depositing thin films is known as

solvent evaporation. It involves the preparation of a colloidal suspen-

sion of metal oxide particles dispersed in a volatile solvent. Such a

colloidal suspension, or colloid, is known as a sol. These sols may

readily wet clean glass or other substrates, and they show a tendency to

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gel when sufficiently concentrated. Thus, when these sols are applied to clean substrates, a thin film of the sol is deposited. The solvent quickly evaporates, which concentrates the sol, and the sol becomes a rigid gel. The resulting film, in the form of a gel, may then be fired to transform the gel into an almost pure metal oxide coating. Films produced by this method are also known as sol-gel coatings. They can be deposited by a variety of methods which will be described in the background section of this paper.

Solvent evaporated films offer some distinct advantages over vacuum deposited films. The most obvious of these is the freedom from a high-vacuum chamber. This would allow for the coating of large optical elements without the need for large vacuum chambers. There would, of course, be a need for an oven large enough to fire the device being coated.

Another advantage of solvent evaporated films is their superior microstructure. Complete pore closure can be accomplished during the firing process (11:1847). Thus, the films do not tend to absorb water vapor, for the case of complete pore closure, when exposed to humidity. This is an extremely difficult problem to overcome in the vacuum deposition process, resulting in a change in the refractive index of the exposed layers when water vapor is absorbed.

The method of solvent evaporation offers an alternative, yet effective, means of depositing thin film coatings on optical substrates. The The remainder of this report focuses on the preparation of thin film coatings on glass as well as the measurement of the optical constants and performance of coatings produced by solvent evaporation. In the following section, a brief history and background of solvent evaporation

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will be covered. The method of sol preparation and the coating process will be presented in the experimental section. A section on results and discussion follows, ending with conclusions and recommendations.

II. Background

Coatings produced by the sol-gel method are by no means new. In fact, sol-gel products have been on the market for more than 20 years. Some of these commercial products are a part of everyday life.

The early work on sol-gel coatings was published primarily in patent literature. There is, however, some journal literature available which describes the history of the sol-gel process. Dislich and Hinz have written at least two papers (1;2) which discuss the evolution of sol-gel coatings and gel technology in general, some of which is given below.

The first investigations involving metal oxide coatings on glass via sol-gel processes were performed by Geffcken and Berger. This work was reported in 1939. Since then, a number of products have appeared employing sol-gel coatings. Large scale production of automotive rear view mirrors with sol-gel coatings began in 1959. In 1964, antireflective coatings on glass panes were marketed. Sun-shielding windows with tradenames of Calorex and IROX appeared in 1969.

Also in 1969, Schroeder (3) published a treatise on the use of sol-gel techniques for application in thin film physics. This work contained examples of single and multilayer coatings, as well as single and multi-component oxide layers. Schroeder reported that a mixture of two sols containing different oxides could be used to produce coatings with a continuous range of refractive indices. An example is shown in Fig 1. Schroeder reported the ability to reproduce any optical coating or thin film stack of metal oxides that could by made by other means. By doing

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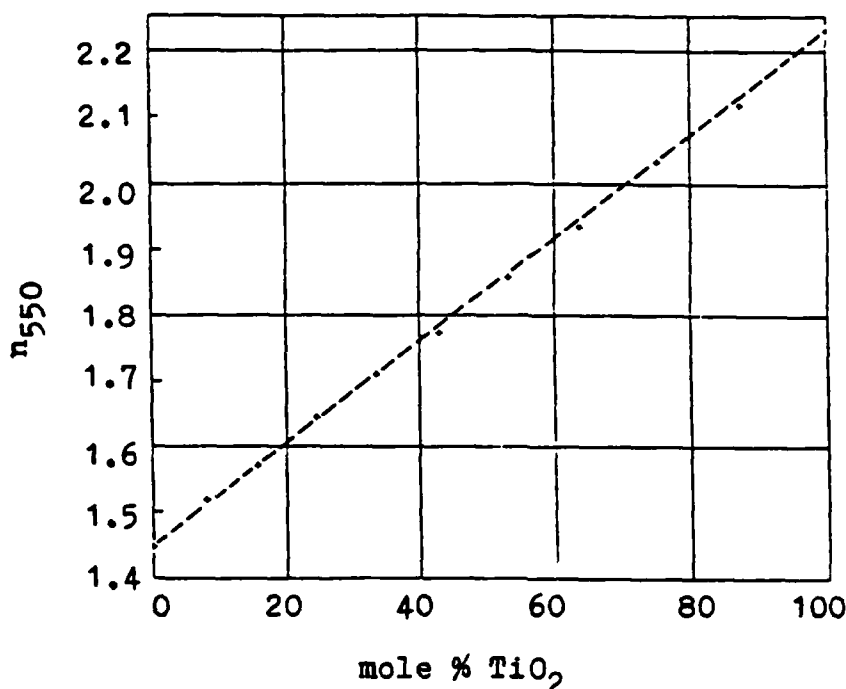
Fig 1. Refractive index of SiO_2-TiO_2 films as a function
of the molar proportion of TiO_2 (λ=550 nm) - after
Schroeder (3:119).

this, he demonstrated the degree of controllability, both in thickness

and refractive index, that is possible by sol-gel techniques.

Sol-gel coatings have been deposited primarily by four processes.
See Fig 2. The most widely used process is the dipping method, where
substrates are dipped and subsequently withdrawn from colloidal suspen-
sions containing metal oxides. A good description of the dipping pro-
cess is given by Schroeder (3:90-93).

A second process, similar to dipping, is the lowering process where
the substrate to be coated remains stationary while the liquid level is
lowered (3:90). This process offers some advantages over the dipping
process since the liquid level can be lowered very smoothly. Oddly

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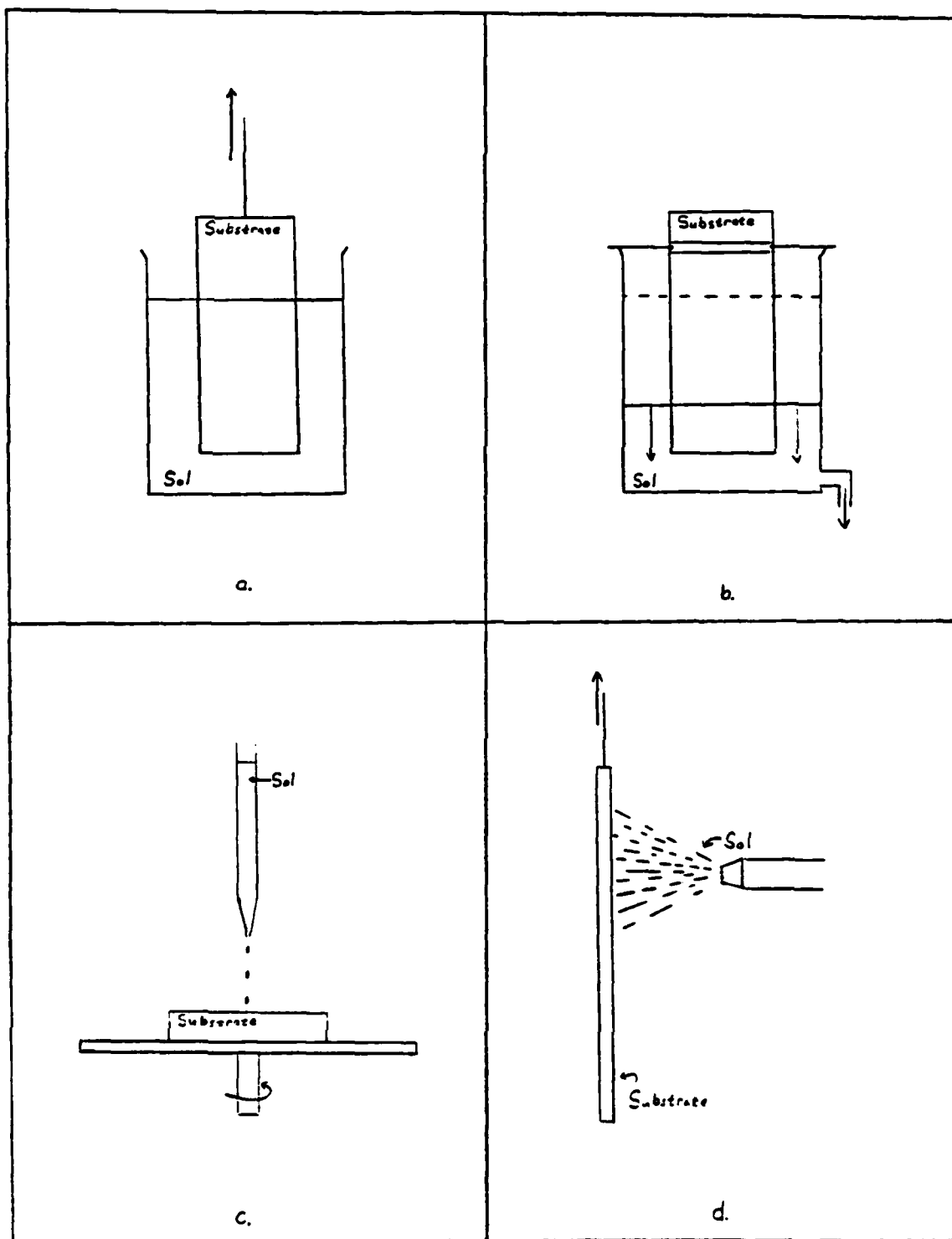
Fig 2. Four processes for depositing sol-gel coatings:
        a) dipping, b) lowering, c) spinning, and d) spraying.

enough, however, this process is not discussed nearly as much as the dipping process. The dipping and lowering processes are both suitable for flat substrates, and the parameters affecting film thickness are identical in both cases. This will be discussed further in the next section.

A third process, more suited to circularly symmetric substrates, is the spin process. Here, a coating is applied by spinning a wetted sur- face at high angular velocities to spread a thin film across the surface. This is usually done by dripping a few drops of a coating solution on the center of a spinning substrate. An investigation of the parameters affec- ting the solvent evaporation rate of spin coated films, and an empirical formula relating film thickness to coating parameters, has been reported by Chen (4).

The fourth process for depositing sol-gel coatings is the spray method. This is accomplished by spraying a fine mist of coating solution onto a substrate. The process is limited to producing protective and insulating coatings where film uniformity is not crucial to coating per- formance. An example of the use of spraying processes is the work of Noguchi and Mizuhashi, where the effects of substrate temperature on the optical properties of cobalt and chromium oxide films were investigated (5).

A wide variety of metal oxide films can be produced by sol-gel tech- niques. Practically any metal alkoxide can be hydrolyzed to produce a solution of polymerized metal oxide. Table I contains a list of metal oxides that have been deposited in thin film form by sol-gel techniques, and which are transparent in the visible region of the spectrum (3:120).

TABLE I

Characteristics of Metal Oxide Coatings
-after Schroeder (3:120)

Oxide	Preferred starting compound	n @ 550 nm	Absorbing below (nm)	Structure
Al_2O_3	$Al(NO_3)_3 \cdot 9H_2O$,	1.62	~250	Amorph.
	Al-sec-butylate			Cryst.
CeO_2	$Ce(NO_3)_3 \cdot 6H_2O$	2.11	400	Cryst.
HfO_2	$HfOCl_2 \cdot 8H_2O$	2.04 (400 nm)	~220	Cryst.
In_2O_3	$In(NO_3)_3$	1.95	420	Cryst.
La_2O_3	$La(NO_3)_3$	1.78	220	
Nd_2O_3	$Nd(NO_3)_3$	(Inhom.)		
PbO	$Pb(CH_3COO)_2$	(Inhom.)	~380	Amorph.
Sb_2O_4	$SbCl_5$	1.90	340	
SiO_2	$Si(OR)_4$	1.455	~205	Amorph.
SnO_2	$SnCl_4$	(Inhom.)	350	Cryst.
Ta_2O_5	$TaCl_5$	2.1	310	
ThO_2	$ThCl_4$, $Th(NO_3)_4$	1.93	~220	Cryst.
TiO_2	$TiCl_4$, $Ti(OR)_4$	~2.3	380	Cryst.
Y_2O_3	$Y(HO_3)_3$	1.82	≤300	
ZrO_2	$ZrOCl_2$	1.72	340	Cryst.

Of importance in this discussion is the range of useful film properties which can be obtained by sol-gel routes. Films can be produced with refractive indices varying from 1.455 for SiO_2 to about 2.3 for TiO_2.

Film thicknesses up to 300 nm can generally be obtained. When this limit of thickness is reached, films tend to crack and craze. Schroeder discusses the limitations on film thickness in terms of thermal stress and other factors (3:101-105). It is interesting to note, however, that the addition of hydroxypropylcellulose to solutions of SiO_2 has been shown to increase the thickness limit to 500 nm (6:230).

Some additional film properties of interest are adherence, wear resistance, and uniformity. Fired films on clean, smooth glass substrates are extremely difficult to remove. In fact, they can only be removed by polishing or grinding. Sol-gel films are generally found to be highly resistant to scratches and wear (3:101). This is especially true of TiO_2 and ZrO_2 coatings. Film uniformity is dependent on the application process used, but it is sufficient enough to produce useful coatings.

For more information on sol-gel coatings and gel technology in general, the reader is referred to a very comprehensive article by Zelinski and Uhlmann (7). Also, the frequently cited article by Schroeder (3) is an excellent overview on the topic of sol-gel coatings.

III. Theory

The theory for this report will be presented in two parts. In the first part, the basic theory of thin films will be covered. Of interest here is that part of thin film theory by which calculations of transmission spectra of coated substrates can be made. In the second part, the theory of sol-gel coatings will be discussed. This discussion will include the chemistry involved in preparing metal oxide sols, the nature of these sols, and some aspects of the sol-to-gel and the gel-to-metal-oxide transitions. Also, the relationships between film thickness and coating parameters will be presented.

Thin Film Theory

The observable effects of thin films can only be understood on the basis of light interference. Thus, it is necessary to understand that one part of a light wave may interfere with another part, provided the wave has a certain degree of coherence. If these aspects of the wave nature of light are unfamiliar, the reader is referred to chapters 7 and 9 of the introductory textbook by Hecht and Zajac entitled Optics (8).

The best place to start the discussion of thin film theory is with the Fresnel equations. The Fresnel equations can be used to determine the amount of light that will be reflected and transmitted at an interface between two dielectric media. For an uncoated substrate, the reflectance at normal incidence is given by

$$R = \left(\frac{n_s - n_0}{n_s + n_0} \right)^2 \tag{1}$$
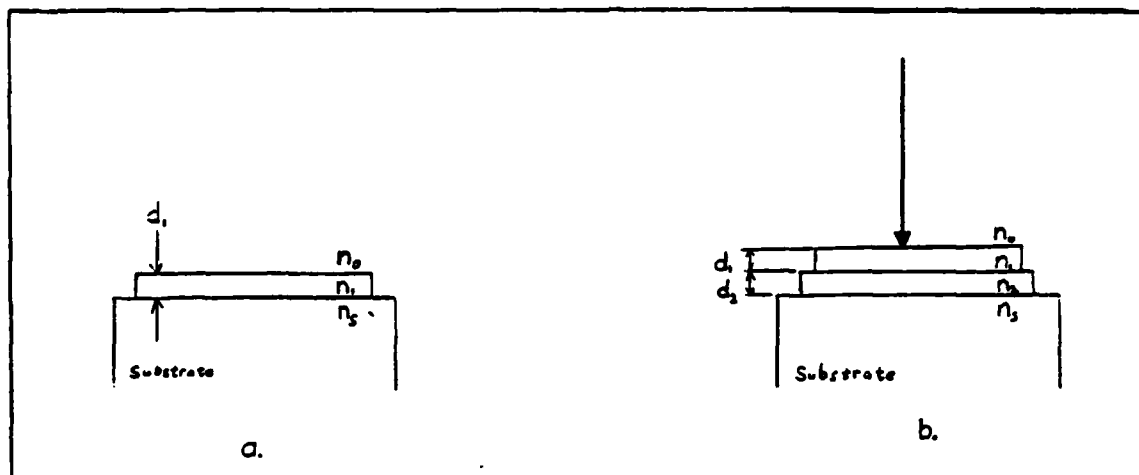
Fig 3. Diagram showing thin films on substrates: a) single
layer and b) double layer showing a light beam at
normal incidence.

where R is defined as the ratio of the reflected to incident light flux,
n_s is the index of refraction of the substrate, and n_0 is the index of
refraction of the incident medium (8:72-81).

For a thin film between two dielectric media, such as air and glass,
a derivation similar to that for the Fresnel equations must be applied at
both the front and back surfaces of the film (8:312-313). Thus, if a
film of index n_1 is added to the surface of a substrate, as in Fig 3-a,
then the reflectance at normal incidence becomes

$$R = \left(\frac{n_0 n_s - n_1^2}{n_0 n_s + n_1^2} \right)^2 \qquad (2)$$

where the thickness d_1 of the layer satisfies the condition

$$\frac{\lambda_0}{4} = n_1 d_1 \qquad (3)$$

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Here, λ_0 is the reference wavelength. Eq (3) is the quarter wave optical thickness condition. For the case of a double-layer, as in Fig 3-b,

$$R = \left(\frac{n_2^2 n_0 - n_s n_1^2}{n_2^2 n_0 + n_s n_1^2} \right)^2 \qquad (4)$$

provided the second layer, of index n_2 and thickness d_2, also satisfy the quarter wave condition (8:314). This can be written

$$\frac{\lambda_0}{4} = n_1 d_1 = n_2 d_2 \qquad (5)$$

If the films and substrate do not exhibit significant absorption, then the following approximation is valid:

$$T = 1 - R \qquad (6)$$

where T is the transmittance, and is defined as the ratio of transmitted to incident light flux (8:80).

It is interesting to note that the reflectance in Eqs (1), (2), and (4) remains the same if the direction of incidence is reversed from that shown in Fig 3-b. In other words, if the light is incident from inside the substrate, through the films, to the surrounding medium, then R is unchanged. This becomes important when substrates are coated on both sides, as in the sol-gel dipping process.

Consider a substrate coated identically on both sides. The details of the coating are not important, so long as the reflectance, at normal incidence, is the same for both front and back surfaces. Let a beam of unit irradiance light be incident normally on one surface with a wavelength at which R is known. The result of multiple reflections is shown

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in Fig 4 where the false bending of the beam inside the substrate is introduced for clarity. The external reflectance, which is the total reflected irradiance divided by the incident irradiance, is given by

$$I_R = \sum_{j=1}^{\infty} I_{R_j} = R + T^2R + T^2R^3 + T^2R^5 + \ldots \qquad (7)$$

$$= R + T^2R(1 + R^2 + R^4 + R^6 + \ldots) \qquad (8)$$

The infinite sum in parentheses is equal to $(1 - R^2)^{-1}$, so

$$I_R = R + \left(\frac{T^2R}{1 - R}\right) \qquad (9)$$

Assuming $T = 1 - R$, the external reflectance becomes

$$I_R = \frac{2R}{1 + R} \qquad (10)$$

Similarly, the external transmittance is

$$I_T = \sum_{j=1}^{\infty} I_{T_j} = T^2 + T^2R^2 + T^2R^4 + T^2R^6 + \ldots$$

$$= T^2(1 + R^2 + R^4 + R^6 + \ldots)$$

$$= \frac{T^2}{1 - R^2} \qquad (11)$$

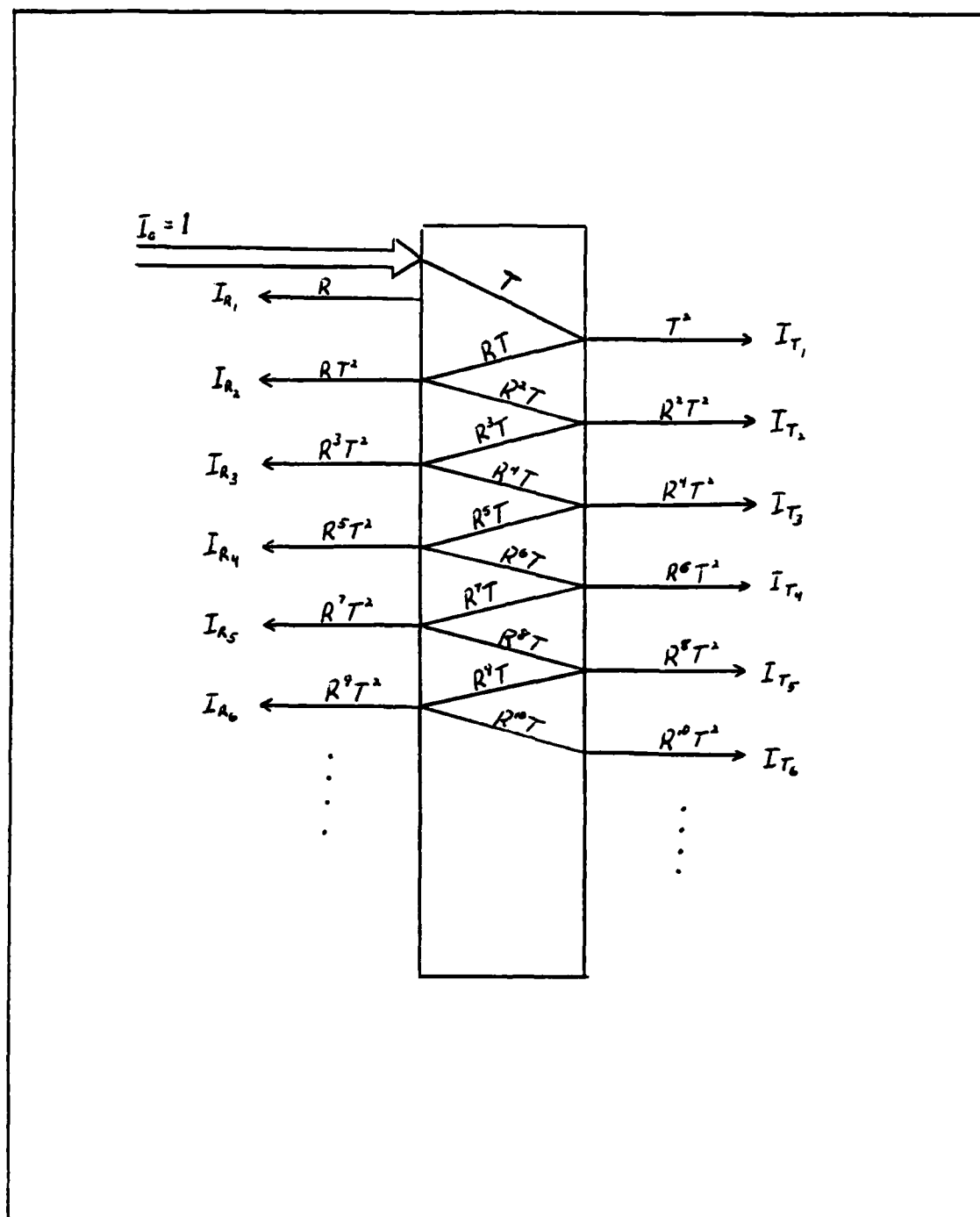Letting $R = 1 - T$,

$$I_T = \frac{T}{2 - T} \qquad (12)$$

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Fig 4. The result of multiple reflections of a normally
incident beam of light on a substrate where the
reflectance is R and the transmittance is T. The
bending of the beam is not real, but is introduced
for clarity.

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Eq (10) or (12) can be used to calculate the transmission spectra for a substrate coated on both sides if R or T is known as a function of wavelength.

To this end, the transmittance as a function of wavelength can be calculated by

$$T = \frac{4n_o n_s}{(n_o B + C)(n_o B + C)^*} \tag{13}$$

where the complex quantities B and C are given by the matrix product

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{ \prod_{j=1}^{q} \begin{bmatrix} \cos \delta_j & \dfrac{i \sin \delta_j}{(n_j - ik_j)} \\ i(n_j - ik_j)\sin \delta_j & \cos \delta_j \end{bmatrix} \right\} \begin{bmatrix} 1 \\ n_s - ik_s \end{bmatrix} \tag{14}$$

and where

$$\delta_j = 2\pi (n_j - ik_j)d_j/\lambda \tag{15}$$

d_j = physical thickness of layer j

$n_j - ik_j$ = optical constants of layer j

$n_s - ik_s$ = optical constants of the substrate

q = number of thin film layers

The wavelength dependence of T is contained in Eq (15). Eqs (13), (14), and (15) can now be used to calculate a theoretical transmission spectrum where the transmitted flux, i.e. the external transmittance, of a substrate coated on both sides would be given by Eq (12). If absorption effects are not present, then the values of the k's in the above expressions are set equal to zero (9:11-12).

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Sol-Gel Theory

The ability to deposit clear metal oxide films from solutions has three prerequisites. First, a suitable liquid precursor must be obtained. Second, the liquid phase of this precursor must have a high evaporation rate so that when a thin film is formed, the solvent will evaporate readily. Finally, the resulting gel must be able to be converted to a glass-like substance. These prerequisites are met by the following:

1. Hydrolysis of metal alkoxides
2. Polycondensation (polymerization)
3. Peptization to a clear sol
4. Solvent evaporation
5. Pyrolysis

In addition, the ability to control refractive index and film thickness is desirable.

Hydrolysis. The first step involves the hydrolysis of diluted metal alkoxides in alcohols. A metal alkoxide has the general formula $M(OR)_\nu$, where M is a metal with valence ν, and OR is an alkoxide group. An alkoxide group is an ionized alcohol molecule. For example, an ionized ethanol molecule forms an ethoxide ion and a hydrogen ion:

$$C_2H_5OH \longrightarrow C_2H_5O^- + H^+ \tag{16}$$
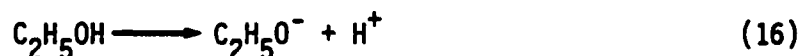
Metal alkoxides react readily with water. The hydrolysis reaction can be represented by

$$M(OR)_\nu + xH_2O \longrightarrow M(OH)_x(OR)_{\nu-x} + xROH \tag{17}$$
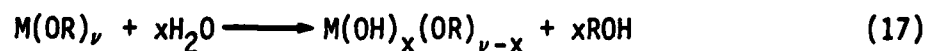
This reaction shows that one molecule of alcohol is formed for each molecule of H_2O that reacts with the metal alkoxide (7:1070)

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```
              OH
              |
       HO  -  M  -  OR
              |
              O         OR        OH        OR        OR
              |         |         |         |         |
       RO  -  M  -  O - M  -  O - M  -  O - M  -  O - M - OH
              |         |         |         |         |
              OR        O         O         O         OH
                        |         |         |
                        M  -  O - M  -  O - M  -  or
                        |         |         |
                        OR        OH        OH
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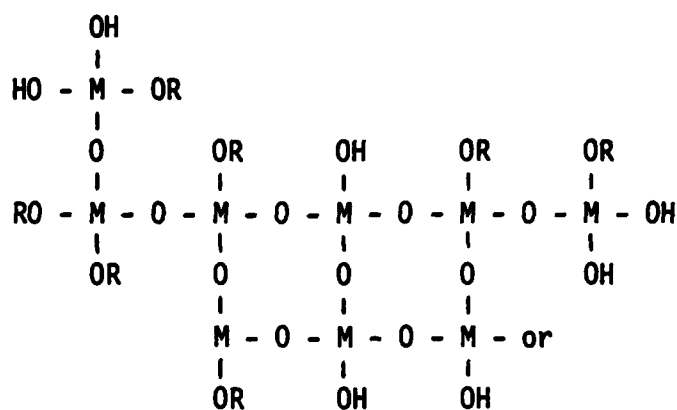
Fig 5. Polymerization showing oxygen bridging and terminal
        hydroxide and alkoxide groups.

<u>Polycondensation</u>. Hydrolysis is followed by polycondensation to form

M-O-M bonds by either of two reactions:

$$-M-OH + HO-M- \qquad -M-O-M- + H_2O \qquad (18)$$

$$-M-OH + RO-M- \qquad -M-O-M- + ROH \qquad (19)$$
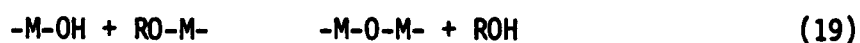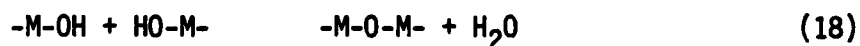
The reactions in Eqs (18) and (19) are what account for polymerization

(7:1070). For example, if the metal in the above equations is a valence

four metal, such as Ti, then -M-O-M- bonds can occur in a three dimen-

sional manner (3:95-96) as in Fig 5, where it must be remembered that the

metal bonding is actually tetrahedral in nature. The structure of the

polymers thus formed depends on many factors which will not be presented

here. A discussion of this is given by Sakka and Kamiya (10).

```

Once the polymerization has proceeded to such a point that the particles have reached colloidal dimensions, then the resulting solution is known as a sol. A sol is a colloidal suspension of solid particles in a liquid. The degree of polymerization depends on the initial concentration of the metal alkoxide and on the rate of hydrolysis. For thin film deposition, the rate of hydrolysis and the alkoxide concentration must be kept small. This is accomplished by highly diluting the alkoxide with alcohol to lower its concentration, and by limiting the amount of $H_2O$ available for hydrolysis (10). Typically, the mole ratio of $H_2O$ to alkoxide is about two (12:2961).

Peptization. The reactions shown in Eqs (18) and (19) will usually not proceed readily unless an acid or base is added as a catalyst. The catalyst also serves to peptize the sol if coagulation occurs. Coagulation typically occurs during the hydrolysis of metal alkoxides, giving the solution a cloudy appearance. Peptization is then necessary to redisperse the coagulated particles, and to transform a cloudy solution into a clear sol. These points are discussed by Yoldas (13).

Solvent Evaporation. At low enough concentrations of water and alkoxide, the sols described above exhibit stable viscosities and tend to gel only when solvent is allowed to evaporate. They can thus be stored in sealed containers for months and even years without gelling, although the viscosity will, in general, increase gradually with aging (12:2961).

Since the sols consist mostly of alcohol, they will readily wet clean glass and other substrates. When substrates are withdrawn vertically from a sol, a film of liquid is dragged upward (14:123). The film

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is thin enough that solvent can start to evaporate as soon as the film is clear of the liquid level.

As stated earlier, metal oxide sols will gel when a sufficient amount of solvent evaporates. The sol-to-gel transition occurs when the sol becomes concentrated to the point that increased crosslinking of the polymers forms a rigid structure throughout the liquid phase. When the solvent evaporation rate is high, as it is for light alcohols, gellation occurs rapidly as a film is withdrawn from a sol. The resulting film, in the form of a gel, has sufficient rigidity to support itself, and no running or draining of the film will occur. If the solvent evaporation rate is low, then some draining of the film will occur. This process, in effect, places another limit on the obtainable film thickness when dipping is used to apply coatings (15:1419).

The gelled film just described is not in a glass-like form. The polymer crosslinking is only sufficient enough to bring about rigidity. Terminal -OH and -OR groups are still attached to some of the metal atoms in the gelled film. Refer to Fig 5. In addition, solvent is still present in the film and must be driven off or allowed to escape.

Gelled films will continue to dry after application, even at room temperatures. This drying refers to continued solvent evaporation, and may proceed until all volatile substances have evaporated from the film. Terminal -OH and -OR groups, however, are not removed during drying since this requires additional energy (11:1845).

Pyrolysis. The final step in producing metal oxide films is to transform the dried gel into a glass-like substance. This is done by supplying energy, in the form of heat, to thermally decompose and drive off the terminal groups. It is even possible for the reactions of Eqs

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(18) and (19) to continue, leading to increased oxygen bridging, and, consequently, increased densification. This dried gel to metal oxide transition is referred to as pyrolysis. The temperature range at which pyrolysis occurs is approximately 250-600°C (11:1845-46).

Control of Refractive Index. The refractive indices of metal oxide films produced by sol-gel techniques are generally the same as those of films produced by other methods. It is possible, however, to control the refractive index in a number of ways. Incomplete densification during the firing process leads to lower indices. This can be accomplished by using short baking periods and lower baking temperatures to keep the density down. The production of high porosity films is another way of lowering the density (16). As stated in Section II, by mixing two sols together, it is possible to vary the index of refraction continuously between two values. This is yet another way in which index of refraction can be controlled.

Control of Film Thickness. Film thickness is determined by properties of the substrate and coating solution, and by parameters of the application process. These factors can be broken down in the following manner as suggested by Yoldas (17):

1. Nature of the solution
2. Nature of the substrate
3. Application method and rate
4. Drying conditions
5. Heat treatment conditions

To discuss all of these factors in detail would be exhaustive and would require much theory that will not be presented. The course taken here will be to present only those factors which are most important to thickness

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control for vertical withdrawal from solutions. It should be noted that no theoretical model has yet been developed that accurately predicts film thickness on the basis of the above mentioned factors.

The property of the solution, or sol, that most affects film thickness is viscosity. Film thickness is directly related to solution viscosity and can be seen from the fact that viscosity is a frictional force between fluid molecules. In the withdrawal process, a thin film is dragged upward; and, the greater the viscosity, the greater the thickness of the film that will be pulled upward. The importance of solution properties is diminished if sols can be prepared whose properties do not vary significantly with time or with variations in external factors such as temperature (3:90-91). For this reason, properties of the prepared sols were considered to be constant in this investigation.

The properties of the substrate that affect film thickness are smoothness and wettability. These properties of the glass substrates used in this investigation were also assumed to be constant from sample to sample.

In the withdrawal process, the rate of withdrawal significantly affects film thickness. The withdrawal rate is what is used to vary film thickness when a stable sol has been prepared, and when all other factors are constant. Film thickness is directly proportional to withdrawal rate. The functional relationship between thickness and withdrawal rate will be presented at the end of this section.

Finally, the drying and heat treatment conditions affect film thickness by influencing the solvent evaporation rate and the degree of pyrolysis. The ambient air temperature and humidity during the withdrawal process affect solvent evaporation (3:90-91). As stated earlier, the

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solvent evaporation rate has the effect of placing an upper limit on film thickness. Since pyrolysis is associated with film shrinkage due to densification, thickness decreases with the increasing degree of pyrolysis. Yoldas has shown that densification goes almost to completion at temperatures in excess of 300°C (11:1845). It was therefore assumed that these factors were approximately constant throughout this investigation with slight errors being introduced due to uncontrolled humidity.

Functional Dependence of Thickness on Withdrawal Rate. The functional dependence of thickness d on withdrawal rate v is not well understood. All expressions given in the literature are approximations. Schroeder has stated that d is approximately proportional to $v^{2/3}$, which implies the simultaneous effect of gravity as well as viscosity and surface tension of the solution (3:91). It is assumed that Schroeder is referring to final film thickness. Yoldas has claimed that undried film thicknesses can be determined by

$$d = \left(\frac{2v\eta}{\rho g}\right)^{1/2}$$

(20)

where v is the pull rate, $\eta$ is the solution viscosity, $\rho$ is the film density, and g is the acceleration of gravity. A drying factor must be added to this expression (15:1419). (Reference 15 contains an error in the printing of Eq (20). The correct form was obtained from an in-house report cited as reference 18.) In a paper by Yang et al., two more approximations are given. The first, attributed to Landau and Levich, has a $v^{2/3}$ dependence for the thickness of undried films, while the other has a $v^{1/2}$ dependence for dried film thickness (13). The reasons for these differences was not investigated.

# IV. Experimental Procedure

Coatings were applied to glass substrates by vertical withdrawal from prepared sols. After drying and firing, coating properties were measured. Quantitative as well as qualitative observations were made.

## Solution Preparation

The sols were prepared using the method of Sakka and Kamiya (10:33), and the proportions suggested by Yoldas (12:2961). The four ingredients used in carrying out the hydrolysis reaction were a metal alkoxide, an alcohol, diluted hydrochloric acid, and deionized water. In every case, the alcohol used was the alcohol corresponding to that of the alkoxide groups. For example, titanium ethoxide, $Ti(OC_2H_5)_4$, contains ethoxide groups, so ethanol, $C_2H_5OH$, was used as the solvent alcohol.

The concentration of the sol is specified as percent, by weight, of the equivalent oxide content. This means that once the hydrolysis reaction is complete, there will be a certain percentage, by weight, of metal oxide polymers in the sol. Putting this another way, if all the volatile components of the sol were evaporated, the remainder would be the specified percentage of metal oxide. For example, if 100 g of a 2% sol containing $ZrO_2$ were evaporated completely, 2 g of $ZrO_2$ would remain. The equivalent oxide was regulated by the degree of dilution, and was typically in the range of 2 to 4 percent.

The method of Sakka and Kamiya involves diluting the alkoxide with half the specified amount of alcohol, and adding to it a solution containing the proper amount of $H_2O$, HCl, and the other half of the specified amount of alcohol. HCl was added at a concentration of 2 moles per

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liter with $H_2O$ as solvent. It was therefore necessary to keep track of the amount of $H_2O$ added with the acid. See Appendix for a sample of preparation quantities.

The mixing was done by first placing the diluted alkoxide in a beaker under rapid stirring with a magnetic stirrer. The alcohol-HCl-water mixture was then added dropwise, from a buret, to the diluted alkoxide. Typically a dispersed, milky precipitate would form as more and more $H_2O$ was introduced to the diluted alkoxide; but, by the time the buret was nearly empty, enough acid was present to peptize the mixture. The result was usually a clear sol.

Prepared sols were stored in stoppered flasks at room temperature. The most concentrated sols, those greater than 3% equivalent oxide, tended to gel after about three weeks, even when kept in sealed containers. The less concentrated sols, those less than 3% equivalent oxide, retained stable viscosities for more than 2 months when stored in sealed containers. If the sols became contaminated with dust, or if they became too viscous for further use, they were disposed of by allowing them to evaporate completely under a fume hood until they gelled and dried. The resulting gel pieces were then fired to solid oxides.

## Substrate Preparation

The majority of the substrates used in this investigation were ordinary glass microscope slides. They were cleaned by drag wiping both sides with methanol and then applying a number of passes of MC&B brand collodian. The minimum number of collodian passes was two.

Collodian is a solution of pyroxylin, a nitrocellulose, in alcohol and ether. When spread on the surface of a substrate, it dries into a

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thin sheet resembling cellophane. The sheet can be stripped off, taking with it dust particles and organic residues (19).

Following the application of collodian, the substrates were blown dry with a clean, dry gas. This was necessary to remove moisture due to the cooling effect of the evaporation of the collodian solvents. During the entire cleaning process, the substrates were held with a clamp to avoid touching the substrates directly. In most cases, the substrates were cleaned just prior to application of a coating.

## Coating Procedure

Application of a film was done in a three-step process. The first step involved applying a sol to the substrate. Then the resulting film was allowed to dry until it gelled completely. Finally, the coated substrate was fired to pyrolyze the gel. The application of films was done by the withdrawal method in the ambient laboratory atmosphere. The temperature varied in the narrow range of 19.5-22.5°C, and the relative humidity varied in the range of 35-60% from day to day.

Withdrawal. The apparatus for withdrawing substrates from the sols was a simple hoist shown schematically in Fig 6. The hoist was made of aluminum and plexiglass with nylon fishing line connecting the dolly to the crank. The hoist was driven by a variable-speed, reversible motor which engaged the hoist via an O-ring belt. It was necessary to isolate the motor to prevent motor vibrations from disturbing the withdrawal process. This was done by placing the hoist on an isolation table so that the only contact between motor and hoist was through the O-ring belt.

The substrates were attached to the dolly by hooking a removable clamp, the same clamp used in the cleaning process, to a screw on the

Fig 6. Schematic of hoist for withdrawing substrates from solution.

dolly. This allowed easy handling of the clean substrates since the substrates could be held with the clamp and hooked directly onto the dolly without touching the substrates themselves. The substrates were then lowered into a beaker containing a sol and withdrawn vertically.

The rate of withdrawal was determined by timing the dolly as it was raised between two timing marks. The withdrawal rate could be varied continuously by adjusting the speed of the motor. The minimum withdrawal rate for this setup was 1 mm/s.

Drying. Once a sample was dipped and withdrawn, it was left hanging on the hoist for at least five minutes. Some draining did occur so that the bottom of the sample received a thicker coating. The drying process could be extended to longer periods with a corresponding increase in the density of the film.

Firing. The final step in the coating process was accomplished using a small electric furnace. The temperature was measured by a chromel-alumel thermocouple with a reference junction at room temperature. The dried samples were fired up to five at a time on an aluminum rack as shown in Fig 7.

The samples were typically fired at 450°C for 30 min. Usually, rapid heating was used, in which case the samples were placed into the hot furnace (450°C) and brought up to temperature rapidly. Rapid heating works only for thinner films in which case the shrinkage during pyrolysis is small. Films that are a few hundred nanometers thick tend to crack and craze under rapid heating and must be brought up to firing temperature gradually. Ultimately, there is a thickness beyond which crazing will always occur during the drying process. This ultimate thickness depends on the particular sol being used.

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Fig 7. Aluminum rack showing the upright position in which coated substrates were fired.

## Measurement of Film Properties

The most important properties of a thin film are its physical thickness and index of refraction. Some other properties include the film's adherence to the substrate, its hardness, and its uniformity. The thickness and index of refraction were measured quantitatively while the other properties were measured by purely qualitative means. Coating performance was determined by transmission spectra.

Physical Thickness. The physical thickness was determined using a Sloan Dektac IIA profilometer. This instrument is a stylus device that measures height variations of a surface. It is particularly sensitive to sharp steps, up or down, of the stylus. Thus, it is desirable to produce a step when attempting to measure film thicknesses by this method.

A step can be produced by scratching the film with a sharp tool before the sample is fired. At this point, the film is not as hard or as dense as the glass substrate, and can effectively be scratched through without applying enough pressure to scratch the glass. Once this is done, the film can be fired, or the thickness can be measured prior to firing. The dried films are hard enough so that the stylus does not penetrate the film.

The film thickness is given by the distance that the stylus steps down into the scratched groove. The grooves were typically 100 $\mu$m in width, and the depth was determined by taking an average of five passes through the groove. Each measurement was taken to the nearest 5 nm. The film thickness was measured near where the films appeared to be the most uniform.

<u>Index</u> <u>of</u> <u>Refraction</u>. The refractive index of the films was measured using a Rudolph Thin Film Ellipsometer. An ellipsometer works on the principle that the reflection coefficient and change in polarization of a reflected beam of light are related to the thickness and index of refraction of a film, provided the substrate index is known. A schematic of an ellipsometer is shown in Fig 8. For more information on the use of ellipsometry for characterizing thin films, see Dunlavy et al. (21).

The reflected light that passes through the analyzer of the ellipsometer and into the detector must be from the top surface of the sample only; otherwise, a composite of information from both the front and back reflections will be measured. To ensure that only the front reflection enters the detector, two approaches can be taken. Either the substrates can be chosen thick enough so that front and back reflections are separated

Fig 8.  Schematic of an ellipsometer, after Archer (20).

at the detector, or the back side of thinner substrates can be frosted
to scatter and depolarize the back reflection.  See Fig 9.  Since micro-
scope slides are on the order of 1 mm thick, the latter course was neces-
sary.

Test slides, those used for measuring the index of refraction of the
films, were frosted on one side by rubbing them on a piece of moistened,
150 grit, silicon carbide wet/dry sandpaper.  This process of frosting the
back surfaces of the test slides was sufficient to scatter the back reflec-
tion.  In this way, the ellipsometer could be used effectively to measure
the index of the films.

The first step in the process of measuring the film index was to
measure the real and imaginary parts, n and k, of the substrate's refrac-
tive index.  This can also be done on the ellipsometer.  The sample must
be leveled and the reflected beam must be aligned so that it enters the
detector properly.  Then, the ellipsometer quantities, $\psi$ and $\Delta$, could

Fig 9. Two approaches for eliminating the back reflection in
ellipsomentry:  a) use of thick substrates and b) frosted
backs.

be measured for the substrate.  The values of n and k could then be cal-

culated from $\psi$ and $\Delta$ with the help of a computer program.

Since the transmission spectra of a sample cannot be measured directly

if one side of the substrate is frosted, the following procedure was used.

A frosted test slide of known index was coated using the procedure described

above.  Another slide was then cleaned and coated on both sides under iden-

tical conditions.  The physical thickness and index of refraction were

measured for the test slide, and it was assumed that a similar coating was

produced on the corresponding sample.  One disadvantage of this technique

is that n of the substrate varies in the second decimal place from slide to

slide.  This, however, did not prove to be a significant problem, since an

average value of n, taken over many substrates, was used in calculating the

theoretical transmission spectra.  A good correlation with measured spectra

was achieved.

Once the test slide was coated, $\psi$ and $\Delta$ were measured again on the

ellipsometer.  Since the physical thickness d was obtained with the

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profilometer, and since n and k of the substrates had previously been measured, n and k of the film could be calculated with a computer program. It is not necessary to know d in advance, but it speeds up the calculation immensely.

_Transmission Spectra_. The transmission spectra of coated samples were obtained with a Cary 14 spectrophotometer. The UV absorption edge for the substrates was determined to be about 300 nm. Therefore, the spectral wavelength range that was scanned started at 300 nm and continued into the IR region. In this way, the entire visible range was covered.

_Other Film Properties_. Some qualitative observations of film properties were also made. Of these observations, film adherence, hardness, and uniformity will be discussed.

Film adherence is often measured by the tape test. This involves applying tapes, with varying degrees of adhesive strength, to the films, and then peeling them off to see whether the film comes off. There is also the eraser test where an eraser is pressed on the films to see if they can be rubbed off. Neither of these tests would have been severe enough to remove the films produced by the above method. This was evident after performing the following tests.

In the first test, a sharpened steel point was used to pick at the edge of the films and to see if the films could be lifted away from the substrate. This did not prove to be effective in any way. It was virtually impossible to remove the films by anything short of grinding.

To illustrate the degree of bonding that the films exhibited, the following was done. A sample coated with titanium oxide was broken and

the glass shards were examined to see if the film had flaked off. What was found were a few pieces, approximately 100 $\mu$m thick, that had fractured parallel to the surface of the substrate. Since the film thickness was orders of magnitude thinner than these pieces, it appeared that the film was bonded so tightly to the substrate that the bond strength of the substrate itself was less than the bond strength at the film-substrate interface.

The hardness of the fired films was tested by scratching with a sharpened steel point. More pressure was needed to scratch the film than was necessary to scratch the substrate. In addition to being scratch resistant, the coatings were also crack resistant. The samples could be flexed, to a point where the substrates fractured, without any cracking of the films.

Uniformity of the coatings was tested by noting the degree of homogeneity of the color effects produced by light interference. A coating must be of uniform thickness if the apparent color is the same from one point to another when viewed from the same angle. Slight variations in color did occur from point to point with an abrupt thickening of the film at the lower edge. However, there was usually a region in the center of the samples which was free from color variations.

# V. Results and Discussion

The results of this investigation show that sol-gel processes can be used to produce useful interference coatings. This is seen especially by the productions of an antireflection coating using a double-layer design. In this section, data will be presented concerning sol stability, the functional relationship between film thickness and withdrawal rate as determined by experiment, and the transmission spectra of samples as compared to theoretical spectra. Some discussion on the validity of omitting absorption will end the section.

## Sol Stability

Stable sols were obtained only at concentrations below 3% equivalent oxide. This can be seen by the experimental results summarized in Table II. The only factor that was varied in preparing these sols was the alkoxide concentration. In all cases, the $H_2O$/alkoxide ratio was kept at two. Also, the HCl/alkoxide ratio was kept at 0.05 in all cases. By varying these last two ratios, it may be possible to produce stable sols with higher concentrations. Yoldas has stated that stable sols with concentrations in the range of 1-5% equivalent oxide by weight should be obtainable (12:2961).

## Thickness vs. Withdrawal Rate

The functional relationship between thickness d and withdrawal rate v was determined experimentally. Expressions found in the literature which relate these two quantities either are not very accurate, or they contain parameters that must be obtained experimentally. For these reasons, the simplest approach was to obtain an experimental plot of d vs. v for each

## Table II

## Sol Characteristics

| Metal Oxide | Eq. Oxide Concentration | Stability in Sealed Container |
|---|---|---|
| $ZrO_2$ | 2% | Stable after 1 week* |
| $ZrO_2$ | 2.5% | Stable after 4 weeks |
| $ZrO_2$ | 3.7% | Gelled after 48 hours |
| $ZrO_2$ | 20% | Uncontrolled hydrolysis** |
| $TiO_2$ | 2% | Stable after 6 weeks |
| $TiO_2$ | 2.5% | Stable after 3 weeks |
| $TiO_2$ | 3.7% | Gelled after 4 weeks |

*This sol was disposed of after being contaminated with dust.

**A clear sol was not obtained at this concentration. Peptization did not occur and the entire mixture coagulated.

particular sol. An example is shown in Fig 10. The data was fit, by least squares, assuming a function of the form

$$d = \alpha v^\beta \tag{21}$$

which can be put into linear form as

$$\ln(d) = \beta\ln(v) + \ln(\alpha) \tag{22}$$

The parameters $\alpha$ and $\beta$ are then characteristic of a particular sol. The preceding analysis assumes that all factors affecting film thickness, except v, are approximately constant from sample to sample.

Fig 10. Dependence of film thickness on withdrawal rate as determined experimentally.

The values of $\alpha$ and $\beta$ for the sols in Fig 10 are shown in Table III. A $v^{1/2}$ dependence is suggested by the values of $\beta$ obtained; however, this data is not conclusive. The value of $\alpha$ should be related to viscosity and other sol properties.

## Experimental vs. Theoretical Spectra

A number of coated substrates were produced which exhibited transmission spectra closely resembling the theoretical spectra, assuming no absorption. Single layers of $ZrO_2$ and $TiO_2$ were applied, and the optical

## Table III

### Curve Fitting Parameters for the Sols in Fig 10

| Sol | $\alpha$ | $\beta$ |
|-----|------|-------|
| $ZrO_2$ | 44.43 | 0.487 |
| $TiO_2$ | 17.94 | 0.557 |

properties, thickness and index, were measured. The theoretical spectra, based on the optical properties of films and substrates, was compared to the experimental spectra. In addition, an antireflective coating was successfully produced consisting of a double layer of $ZrO_2$ on $TiO_2$.

Single Layers. Examples of the performance of single coatings are shown in Figs 11 through 14. Of particular interest is the close correlation between theoretical and experimental spectra over most of the visible region. The drop off in transmission exhibited by all samples near 300 nm is due to UV absorption primarily in the substrates.

Fig 13 shows the spectra of a sample coated with a single layer of $TiO_2$ on both sides. The transmittance of the sample falls to nearly 50% near 450 nm. If absorption does not make a significant contribution to this drop in transmittance, then the sample should function well as a beam splitter.

Double Layers. Antireflection coatings were made by overcoating a $TiO_2$ film, of known performance, with a $ZrO_2$ film. The results are shown in Figs 15 and 16. Although not shown in these figures, the transmittance of a typical substrate is flat across the spectrum, at about 90%, except

Fig 11. Spectrum of sample coated with $ZrO_2$: $n_s=1.50$, $n_1=1.82$, and $d_1=125$ nm.

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Fig 12. Spectrum of sample coated with $ZrO_2$: $n_s=1.52$, $n_1=1.82$, and $d_1=113$ nm.

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Fig 13. Spectrum of sample coated with $TiO_2$: $n_s=1.52$, $n_1=2.26$, and $d_1=53$ nm.

Fig 14. Spectrum of sample coated with $TiO_2$: $n_s=1.51$, $n_1=2.21$, and $d_1=39$ nm.

Fig 15. Spectrum of sample coated with a double layer of $ZrO_2$ on $TiO_2$: $n_s=1.52$, $n_1=1.81$, $d_1=58$ nm, $n_2=2.39$, $d_2=43.9$ nm.

below 350 nm where it drops off drastically. The transmittance of substrates is zero below about 300 nm.

The antireflection coatings were made by attempting to match the optical thicknesses of the two layers. The optical thickness of the bottom $TiO_2$ layer was measured and the required optical thickness of the $ZrO_2$ layer was determined. Based on the average index of refraction obtained for $ZrO_2$ layers, the appropriate withdrawal rate was chosen using the information of Fig 10.

### Validity of Assuming No Absorption

The difference between the experimental and theoretical spectra were usually not large at wavelengths not near the UV absorption edge. This suggests that absorption in the films and substrates is not large at these wavelengths. In fact, the absorption coefficient of some substrates was measured and found to be less than $0.01$ $cm^{-1}$. Since the absorption coefficient of films was not determined, it is unclear whether or not the inclusion of absorption in the theoretical spectra would increase the correlation between experimental results and theoretical calculations. Some of the error could be accounted for by the uncertainty of the substrate index as discussed in Section IV.

## VI. Conclusions and Recommendations

This investigation has shown that stable sols of $ZrO_2$ and $TiO_2$ can be prepared and stored for more than two months. From these sols, coatings can be produced with reasonably good thickness uniformity using a withdrawal technique. These coatings can be applied, singly or as multilayers, to produce antireflective, or highly reflective, coatings.

Some questions have yet to be answered. For instance, can coatings be applied more uniformly and over larger areas? Would other methods of applying sol-gel coatings have advantages over dipping? Do the films exhibit significant absorption?

These questions were not completely answered by this investigation; however, observations were made and literature was assembled which hint at the answers to these questions. It should be possible to uniformly coat large, flat elements if a uniform withdrawal rate or drain rate can be maintained. The author's recommendation is to use a draining process to apply films, since it should be possible to lower the liquid level of a sol very uniformly without too much sophistication. This is not the case with dipping, however. It is difficult to obtain uniform pull rates and, at the same time, to completely isolate the sol and sample from external vibrations. The degree of thickness uniformity that is obtainable needs to be determined along with a comparison between methods. Along this same line, the aspects of repeatability need to be investigated.

The absorption of sol-gel films also needs to be measured. This could be done by taking both transmission and reflection spectra, or it could be done using ellipsometry. A comparison of experimental spectra

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with theoretical spectra including absorption would also give an indication of the absorption properties.

A final recommendation, which would make further investigation less troublesome, involves substrates. Ellipsometry on thin substrates is uncertain at best. Choosing substrates which are thick enough so that only the front reflection is seen in the detector of the ellipsometer leads to less difficulties and uncertainties than does frosting the backs of thinner substrates. It is also desirable to use substrates which have a uniform refractive index profile.

## Appendix: Sample Sol Preparation

If it were desired to prepare a sol containing 2.5% equivalent $TiO_2$, by weight, from $Ti(OC_2H_5)_4$ with the following characteristics:

    190 g total solution

    2 moles $H_2O$/mole $Ti(OC_2H_5)_4$

    0.05 mole HCl/mole $Ti(OC_2H_5)_4$

then the following quantities would be necessary:

    12.25 ml $Ti(OC_2H_5)_4$ = 13.563 g = 0.0594 mole

    1.485 ml 2M HCl = 1.485 g = 0.00297 mole
        (this quantity of 2M HCl contains 1.38 ml of $H_2O$)

    0.76 ml additional $H_2O$ = 0.76 g (0.119 mole total $H_2O$)

    220 ml $C_2H_5OH$ = 174.193 g

In determining the above quantities, the following was used (22):

    Density of 2M HCl $\simeq$ 1 g/ml

    Density of $Ti(OC_2H_5)_4$ = 1.107 g/ml

    Density of $C_2H_5OH$ = 0.79 g/ml

    Density of $H_2O$ = 1 g/ml

    Formula weight of $Ti(OC_2H_5)_4$ = 228.14 g/mole

    Formula weight of $TiO_2$ = 79.9 g/mole

    Formula weight of $H_2O$ = 18.015 g/mole

    2M solution of HCl $\simeq$ 93% $H_2O$

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Interference coatings of titanium and zirconium oxide were prepared by a solvent evaporation, or sol-gel, process. Solutions of polymerized metal oxides were prepared from the hydrolysis reaction of diluted metal alkoxides. Coatings were applied to ordinary glass microscope slides by vertical withdrawal from the prepared solutions. Films with thicknesses of 25-200 nm were applied with excellent adherence and durability. Refractive indices and thicknesses were measured by ellipsometry. The transmission spectra of coated slides were measured and compared to theoretical calculations assuming no absorption. Quarter-wave layers of zirconium oxide on titanium oxide were produced as an antireflective coating at 465 nm.

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