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Wharton, John James, Jr.

MICROSTRUCTURE RELATED PROPERTIES OF OPTICAL THIN FILMS

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MICROSTRUCTURE RELATED PROPERTIES
OF OPTICAL THIN FILMS

by
John James Wharton Jr.

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

1984
As members of the Final Examination Committee, we certify that we have read
the dissertation prepared by John James Wharton, Jr.
entitled _Microstructure Related Properties of Optical Thin Films_
and recommend that it be accepted as fulfilling the dissertation requirement
for the Degree of Doctor of Philosophy.

_H. A. MacLeod_  
_Dissertation Director_  
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ABSTRACT

Both the optical and physical properties of thin film optical interference coatings depend upon the microstructure of the deposited films. This microstructure is strongly columnar with voids between the columns. Computer simulations of the film growth process indicate that the two most important factors responsible for this columnar growth are a limited mobility of the condensing molecules and self-shadowing by molecules already deposited.

During the vacuum deposition of thin films, the microstructure can be influenced by many parameters, such as substrate temperature and vacuum pressure. By controlling these parameters and introducing additional ones, thin film coatings can be improved. In this research, ultraviolet irradiation and ion bombardment were examined as additional parameters. Past studies have shown that post-deposition ultraviolet irradiation can be used to relieve stress and reduce absorption in the far ultraviolet of silicon dioxide films. Ion bombardment has been used to reduce stress, improve packing density, and increase resistance to moisture penetration.

Three refractory oxide materials commonly used in thin film coatings were studied; they are silicon dioxide, titanium dioxide, and zirconium dioxide. Both single-layer films and narrowband filters made of these materials were examined. A 1000-watt mercury-xenon
lamp was used to provide ultraviolet irradiation. An inverted magnetron ion source was used to produce argon and oxygen ions.

Ultraviolet irradiation was found to reduce the absorption and slightly increase the index of refraction in zirconium oxide films. X-ray diffraction analysis revealed that ultraviolet irradiation caused titanium oxide films to become more amorphous; their absorption in the ultraviolet was slightly reduced. No changes were noted in film durability.

Ion bombardment enhanced the tetragonal (111) peak of zirconium oxide but increased the absorption of both zirconium oxide and titanium oxide films. The titanium oxide films were found to become amorphous with even slight ion bombardment. Little effect was noted in silicon oxide films.
CHAPTER 1

INTRODUCTION

Thin film coatings are used for a variety of purposes in optical systems. For example, it is possible to design assemblies of thin films that will reduce the reflectance from a surface and thus increase the transmittance of the component. Thin film assemblies, or "stacks," can also be designed to increase the reflectance from an optical component. An example of this is the dielectric stacks used to increase the reflectivity of the mirrors in a high-energy laser cavity. In fact, thin film coatings can be designed to increase the reflectance in one wavelength region while reducing the reflectance for other wavelengths. Such designs can be quite complex, and today the computer is often used to tailor-design coatings required for a specific application.

In the design of thin film assemblies, individual layers are assumed to be continuous and homogeneous. Thus, for each layer the designer assumes only two variables, refractive index and thickness. In fact, however, individual layers are found to be porous and nonuniform. Because of the large number of parameters that must be controlled during the deposition of a single layer, early efforts in multilayer deposition relied heavily on the skill of the operator in producing a film structure that approached the design goal. Anything short of that goal was considered to be a lack of control of the
deposition parameters, especially control of layer thickness. In addition, thin film assemblies behave poorly when exposed to the atmosphere. The drift of interference filters has been observed for some time. In certain applications, the behavior of thin films is considerably worse than the behavior of the bulk materials. For example, the laser-induced damage thresholds of thin film coatings used to increase the reflectivity of the mirrors in a laser cavity have been found to be more than an order of magnitude lower than the bulk material damage thresholds (Walker, 1980).

We now understand that the problems are inherent in the nature of the films themselves rather than errors in their production. Advances in electron microscopy have revealed that optical thin films produced by evaporation are strongly columnar in nature with voids between the columns. This microstructure determines the optical and physical properties of the film, and current efforts are designed to determine how the microstructure depends on the deposition conditions. Several models have been used to relate structure to various parameters. Movchan and Demchishin (1969) showed that one important parameter was substrate temperature. Thornton (1974) added gas pressure inside the coating chamber as an additional parameter to the Movchan-Demchishin model. By varying these parameters as well as adding additional parameters such as electron bombardment during the coating process, it is hoped that thin film properties can be improved.

This research effort has concentrated on modifying thin film coatings by adding energy to the film materials during deposition. Previous work has indicated that post-deposition ultraviolet (UV)
irradiation modifies thin film properties. Bradford et al. (1965) have demonstrated that UV irradiation of silicon oxide films eliminates their high UV absorption and changes their refractive index, thickness, and weight by as much as 10%. Mickelsen (1968) has shown that UV irradiation of silicon oxide films reduces the instabilities of their dielectric properties. Hodgkinson and Walker (1973) have found that UV irradiation reduces the stress in silicon oxide films. Hass et al. (1980) have investigated the decomposition of zinc sulfide when exposed to intense UV solar radiation. Such evidence indicates that UV irradiation during deposition should be studied in the hope of improving the optical and physical characteristics of thin films.

Recent work with ion bombardment during deposition has also shown marked effects upon thin films. Allen (1982) has demonstrated that bombardment with oxygen ions can change the oxygen content of several oxide films. Ebert (1982) has examined how low energy oxygen ions reduce residual absorption in oxide films. Martin et al. (1983) have shown that the density of the columns in growing oxide films can be increased with ion bombardment, resulting in a reduction of the adsorption of moisture in the films. Thus, ion bombardment during deposition appears to be another area that should be studied closely. This research effort has examined aspects of both UV irradiation and ion bombardment.

The next chapter of this paper begins with a discussion of the columnar theory of thin film growth and covers some of the optical and physical characteristics consistent with this model of microstructure. Recent studies of moisture adsorption and electron bombardment
are also discussed, followed by a review of post-deposition UV irradiation and ion bombardment. The following chapter describes the experimental equipment used for this investigation, as well as substrate preparation and materials used. Next follows a discussion of methods of analysis on both the macroscopic and microscopic levels. Following this, the results of this research are covered. Finally, the conclusions drawn from this work and suggestions for future work are reviewed.
CHAPTER 2

BACKGROUND

Optical thin films are used to modify the optical properties of surfaces. Perhaps the oldest application is coating the front surface of glass with a metal in order to produce a mirror. In this case, the metal film is thicker than the skin depth of electromagnetic radiation and the resulting mirror appears optically to be solid metal. However, for most applications, thin films are made thin enough that interference is the most important effect. In fact, a film is said to be thin if interference effects are important and thick if they are not. For most optical applications, films are considered thin and the substrates are considered thick. It should be noted that this criterion depends not only on the physical thickness of the film layers but also on the wavelength of the electromagnetic radiation being used.

By combining thin film layers of materials with both high and low indices of refraction, a variety of thin film optical filters can be constructed. Examples of these are anti-reflection coatings, high-reflectance coatings, edge filters, and band-pass filters. A thorough description of the basic theory of such coatings is given by Macleod (1969), who also describes several aids to the design of such filters. However, calculating the optical properties of a coating consisting of many layers over a given range of wavelengths is very time consuming.
and is best done by computer. The computer can also be used to calculate the inverse, that is, determining a thin film design that will have a required spectral performance over some wavelength range. It has been shown that a Fourier transform method can be used to design multilayer coatings with almost any desired spectral transmittance curve, even one following the shape of the Parliament Buildings in Ottawa, Canada (Dobrowolski and Lowe, 1978).

Rarely, however, do multilayer coatings perform as designed. Because of the many parameters that must be controlled during the vacuum deposition of thin films, the failure of a multilayer coating to meet the design goal had been thought to be a failure in the control of one or more deposition parameters. Great emphasis was placed on the skill of the vacuum plant operator, and improvements in multilayer coatings followed a generally empirical approach that concentrated on improved control of deposition parameters and improved monitoring techniques (Macleod, 1982).

It is now known that the main problem lies in the nature of the thin films themselves. In the design of multilayer coatings, each thin film layer is assumed to be a continuous, homogeneous slab of material that has the same characteristics as the material in bulk form. However, it has long been known by optical coating people that voids are present in dielectric materials deposited in the form of thin films. The term "packing density" has been used to describe the degree to which voids are present; it is simply the ratio of the volume of the solid part of the film to the total volume of the film.
Because of the presence of the voids, it is possible to explain the drift of optical filters placed in a humid environment as the adsorption of water vapor in the voids.

The first person to correlate the adsorption of moisture to the microstructure of thin films was Koch (1965), who used an optical technique to measure the drift of magnesium fluoride layers. He noted that some of the adsorbed moisture, which he called "irreversible," did not desorb when the film was returned to a vacuum. Relying on earlier studies of the size and shape of the grains in very thin metal films, he attributed this irreversibility to the chemisorption of the first monolayer of water over the surface of spherical grains in the film. However, advances in electron microscopy have shown that the principal structure of dielectric thin films is strongly columnar, as shown in Figure 2-1 (Guenther and Pulker, 1976). Voids exist between these columns and contribute to the penetration of moisture.

The adsorption of moisture affects films in a number of ways. The optical properties are changed when voids with an index of refraction of 1.0 are filled with water, which has an index of 1.33. A calculation of the exact index of refraction of the resulting film is difficult, particularly when the packing density is high. For low refractive indices, as in magnesium fluoride, Harris et al. (1979) show that a linear interpolation between \( n_m \), the index of the film material, and \( n_v \), the index of the voids, is accurate. The resulting index is given by the equation

\[
\text{n} = \rho n_m + (1-\rho) n_v
\]
Figure 2-1. Micrograph of columnar structure of thin film.

(From Guenther and Pulker, 1976.)
where $\rho$ is the packing density. For higher refractive indices this relationship is not accurate, and for intermediate packing densities the relationship

$$n^2 = \frac{(1-\rho)n_v^4 + (1+\rho)n_v^2n_m^2}{(1+\rho)n_v^2 + (1-\rho)n_m^2}$$

originally given by Bragg and Pippard is more accurate. For very high packing densities, i.e. above 0.9, the original linear relationship is better. The refractory oxides that are commonly used in optical coatings often do not exhibit a stable index of refraction. They have packing densities just below 0.9, which is the transition region between the two models. For comparison it should be added that the packing density of closely packed columns is 0.903.

A number of attempts have been made to explain how moisture fills the voids in thin films. For a single layer, the adsorption can be simply explained by capillary condensation. However, for multilayers the penetration of moisture can occur either within minutes or over a period of months. Ogura (1975) has found that there are indeed pores within thin films and that the number of pores decreases with increasing film thickness while the diameter of the pores remains much the same. He has also noted that boundaries within films, such as found between two thin film layers, impede the adsorption of moisture within the film. Lee (1983) concurs with this observation and proposes the following model for moisture penetration. A monolayer of moisture immediately spreads over the surface of a film when it is removed from the vacuum coating chamber. The moisture then
penetrates into the film by way of central pores that fill by means of capillary action, or by means of defects in the films such as impurity sites. Moisture spreads through a single film layer at a rate that depends on the density of the film. For example, ZrO₂ has a very porous structure with a low packing density, and moisture penetrates very rapidly through this material. SiO₂ on the other hand has a much higher packing density and acts as a barrier to the penetration of moisture. Lee observed the spread of moisture by constructing narrowband filters and watching the shift of peak wavelength of the filter as moisture penetrated within the structure. This shift is due to a change of the index of refraction of the film as moisture fills the pores, and this technique has proved to be a sensitive means of monitoring moisture penetration.

The columnar structure also has an effect on the mechanical properties of films. The columns support each other, and the greater the support, the greater the durability of the films. It has been observed that increasing the substrate temperature increases the durability of films, and this can be related to the increase in packing density at higher substrate temperatures. Stress is an additional mechanical property that has been measured in thin films, and is related to the structure of the films. The stress can be divided into two parts: an intrinsic component and a component related to the differential contraction of two film materials as they are cooled. According to Macleod (1982), Hoffman has formulated a theory of intrinsic stresses that depends on the boundaries of columnar grains and
the mutual attraction of the columns. Hoffman attributes the surface energy of the columnar surfaces and the gaps between the columns as the most important factors. Adsorption of moisture reduces the surface energy of the columns and changes the forces exerted by the columns upon each other. Thus stress and film durability are decreased by moisture adsorption between the columns. Relating this columnar structure to the various parameters associated with vacuum deposition is thus quite important.

When thin films are deposited by vacuum deposition, there are primarily three separate steps. The first of these is the transition of the source material from a condensed phase, usually solid, to a gaseous state. This transition can be treated either as a macroscopic phenomenon based on thermodynamics or as an atomistic phenomenon based on the kinetic theory of gases. The thermodynamic treatment allows for an understanding of evaporation rates and the interaction between evaporants and their containers; the atomistic approach yields information regarding individual molecules, such as their energy. Aspects of both thermodynamic and kinetic theories as they relate to vacuum deposition are covered in detail by R. Glang (Maissel and Glang, 1970).

The second step of vacuum deposition is when the source vapor travels from the evaporation source to the substrate. Based on a knowledge of the distribution of kinetic energies of molecules in the gaseous state, the spatial distribution of evaporated particles can be derived. It is found that the molecules travel in a straight line, and
the distribution of particles by direction follows a cosine law of emission equivalent to Lambert's law in optics. According to this cosine law, the emission of material is not uniform in all directions, but favors the direction normal to the emission surface, where the cosine has its maximum value. As a result, the evaporation of material from a point source on a spherical surface results in a uniform coating everywhere on the spherical surface.

The final step of vacuum deposition is the condensation of the vapor upon arrival at the substrate. Thermodynamically, the only requirement for condensation is that the partial pressure of the evaporant in the gaseous phase be equal to or larger than its vapor pressure in the condensed phase. This assumes that the condensation takes place on film material already condensed or upon a substrate made of the same material. When the substrate is made of a different material, a third phase must be considered. In this phase, the evaporant atoms are adsorbed onto the substrate but have not yet combined with other adsorbed atoms. The formation of clusters of these atoms is called nucleation, and many models have been proposed to describe this nucleation and the subsequent growth of thin films (Maissel and Glang, 1970). A recent review of growth models (Vook, 1982) found that the most common form of growth of real films is a three-dimensional island-forming process described by the Volmer-Weber model. In this model, the initial process of nucleation begins with mobile adatoms diffusing over the surface of the substrate. Although some of these atoms may desorb, others will collide with additional adatoms to form
clusters that become stable. Continued deposition then results in an increase in the size of the clusters until a maximum cluster density is reached.

The relationship of evaporation parameters to thin film nucleation and growth is important if the goal is improved optical and physical performance of the films. One of the most important parameters affecting the structure of both metal and dielectric films is substrate temperature. Movchan and Demchishin (1969) demonstrated that it is the ratio of substrate temperature to the melting point of the evaporant, $T_s/T_m$, that is important. For values of this ratio below about 0.45, as is the case for almost all thin film deposition, the structure is found to be strongly columnar with the columns running across the film in the direction of growth. An increase in substrate temperature results in greater surface energies and increased mobility of the adatoms, which in turn allows them greater mobility. The resulting columnar structure has a higher packing density, which increases the durability and hardness of the coatings. Typical substrate temperatures for the vacuum deposition of dielectric materials are $250^\circ$ to $300^\circ$ C.

Thornton (1974) added the effect of gas pressure to the Movchan-Demchishin model. A summary of his findings is shown in Figure 2-2. At values of $T_s/T_m$ around 0.1, higher pressures introduce adsorbed gas atoms to the film, which limits the mobility of the evaporant adatoms. Thus, structures found at lower $T_s/T_m$ ratios persist to higher ratios. At values of $T_s/T_m$ between 0.3 and 0.5, the gas
Figure 2-2. Structural zone model.

(From Thornton, 1974.)
pressure has a more limited effect because of decreased surface adsorption. It should be noted that Thornton used sputtering rather than thermal evaporation. At the lower gas pressures used, the evaporant molecules arriving on the substrate can have greater energy than in thermal evaporation; thus, the critical substrate temperature assumes lower values. Under correct conditions it is thus possible to produce films with a higher packing density using sputtering rather than thermal evaporation.

Closely related to gas pressure is the oxygen content within the coating chamber when refractory oxides are evaporated. These oxides, such as ZrO₂, TiO₂, and SiO₂, lose oxygen during the evaporation process, and the resulting films are more absorbing than the bulk form of the same materials. Thus, it is a common practice to add oxygen to the coating chamber during deposition of these materials so that oxygen molecules bombarding the substrate make up for the lost oxygen. However, it is difficult to replace all of the lost oxygen. First, at residual oxygen pressures above about 5 x 10⁻⁴ mbar it is easy to burn out the filaments of the electron guns used for heating the source material. Second, as the residual oxygen pressure is increased above a certain point, the solidity of the films suffers such that it is more important to improve the solidity than to remove the last traces of absorption.

Other important deposition parameters include evaporation rates, the angle of incidence of the vapor stream relative to the substrate, surface conditions on the cleaned substrates prior to
deposition, and the presence of impurities. At this point it should be emphasized that condensation, nucleation, and film growth occur under highly nonequilibrium conditions. That is, condensation rates are very large compared with evaporation rates. Thus it is possible that small changes in deposition conditions will result in appreciable changes in film structure. The fact that a columnar structure has been observed in both metal and dielectric films of both amorphous and crystalline materials indicates that some common feature exerts a very strong influence on the growth of thin films.

The most promising theories hold that the significant factors affecting film growth are a limited mobility of the condensing atoms or molecules in conjunction with a self-shadowing effect due to atoms or molecules already condensed upon the substrate. It has been noted by Nakhodkin and Shaldervan (1972) that the formation of a columnar structure occurs only when the adsorbed atoms have a limited mobility, for example, materials having a high melting point (Cr, Be, Si, and Ge), compound materials having a high binding energy (CdTe, CaF₂, and PbS), and amorphous films. The last category is included because the existence of an amorphous state depends upon a limited mobility. Any change of deposition parameters that results in an increase in mobility, for example an increase in substrate temperature, will eventually eliminate the formation of columns.

The second feature of a self-shadowing effect depends upon the angle of incidence of the vapor stream relative to the substrate. Studies of the angle \( \beta \) formed between the normal to a substrate and
the direction of columnar growth have always revealed an angle less than the angle $\alpha$ formed between the normal to the substrate and the vapor direction. Nieuwenhuizen and Haanstra (1966) were among the first to report on a detailed study of the angle $\beta$ for a wide range of $\alpha$, and found that their results could be described by the equation

$$2 \tan \beta = \tan \alpha.$$  

This equation is now referred to as the "tangent rule." A study of amorphous films by Dirks and Leamy (1977) verifies this rule for all angles, $0 < \alpha < 60^\circ$, and their results are shown in Figure 2-3. Additional studies have revealed that this rule is obeyed by a large number of film materials. This is significant in that intuition would not predict that growing columns would be more normal to the surface than the vapor deposition angle. Since the tangent rule holds true for many materials, it is important to an understanding of the way columns grow.

Numerous computer simulations have been made as an aid to understanding the tangent rule and the effect of limited mobility. As an example, the simulations done by Henderson, Brodsky, and Chaudhari (1974), treat the vapor atoms as hard spheres that "stick" upon reaching the substrate or a sphere already "deposited." If the spheres were to remain in place after sticking, this would be referred to as zero mobility. To take into account a limited mobility, the spheres are allowed to "relax" after initially sticking, but only to the extent than they make contact with the nearest triangular pocket formed by
Figure 2-3. Experimental demonstration of the tangent rule.

The symbols represent data points from different investigators. (From Dirks and Leamy, 1977.)
three spheres. This simulation maximizes tetrahedral packing and results in an amorphous structure. The results agree with the features generally noted in real thin films. That is, a columnar structure is produced with voids between the columns, and the column angle $\beta$ is less than the vapor angle $\alpha$. It is also noted that the column angle $\beta$ and the voids between the columns increase with increasing vapor angle $\alpha$.

A further approximation can be made by using a two-dimensional model in which the vapor atoms or molecules are treated as circles rather than spheres and the point of minimum energy is established when the circle is supported at two points. This is similar to the three-dimensional model in which the spheres are supported at three points. Such a model has been used by Dirks and Leamy (1977), who have found that for the case of zero mobility, the resulting growth is a loosely packed structure consisting of chains that branch out and combine in a seemingly random pattern. If this were a real film, it would have properties very different from that of bulk material. However, when limited mobility is allowed, the resulting structure consists of long dendritic chains that grow away from the structure. These chains have a diameter of several molecules, and show many of the columnar features found in real films. The results of a similar two-dimensional growth simulation by M. Sikkens (Hodgkinson et al., 1983) are shown in Figure 2-4, where the angles of incidence are 0°, 20°, and 40°.
Figure 2-4. Two-dimensional thin film growth simulation.

(a) $\alpha = 0^\circ$. 
Figure 2-4—Continued

(b) $\alpha = 20^\circ$. 
Figure 2-4--Continued

(c) $\alpha = 40^\circ$. 
A more realistic three-dimensional simulation by Leamy, Gilmer, and Dirks (1980) takes into account the range of interatomic forces by also considering the interaction of incident atoms with those atoms in the deposit that are beyond the direct interaction range. In this model, a potential is assigned to each atom, and the atom is considered to be at rest only when all but 0.01% of its initial kinetic energy has been dissipated in the deposit. The results are similar to other three-dimensional simulations although at normal incidence the dendritic chains are replaced by a loosely packed structure with random shaped voids. The case of normal incidence is a rather special case that is never actually achieved for real thin films. First, the source material is never just a point source, and second, substrates are normally rotated during deposition such that the vapor incidence angle is constantly changing.

While it is gratifying that the results of these computer models are in agreement with experiments in that a columnar structure is formed, there is a problem in the size of the columns. In micrographs of real thin films, the columns have diameters of several nanometers; in the computer models, the columns have a diameter of only a few molecules. This is a difference of about two orders of magnitude. An additional problem is that the diameter of the columns is greater for thicker films than for thin films. Lissberger and Pearson (1976) have made shadow replicas of optical coatings and examined them with a transmission electron microscope. They have found that the basic diameter of the columns does not appear to change with
film thickness, and in thick films no transition is noted from a smaller to a larger basic structural unit.

A solution to these apparent contradictions is provided by Messier (1982) and explained by Macleod (1982). Messier and his colleagues have been examining a wide range of thicknesses of films of amorphous germanium and silicon and of silicon carbide. Their analysis has included transmission electron microscopy for very thin films and scanning electron microscopy. They have found that thicker films do have larger structural units than thin films, and by careful observation have been able to explain the transition from one structure to the other. The basic structural unit has a diameter of the same order of magnitude as the dendrites predicted by Dirks and Leamy. This basic unit can be observed using direct electron microscopy of very thin films. The voids between these basic units are of a comparable order of magnitude. As the film thickness increases, the basic structural units do not disappear but combine together to form the larger columns seen in film coatings made for the visible region. The voids within the larger columns tend to close, and are replaced by voids between these larger columns. As the film thickness increases even more, this process is repeated again such that the larger columns combine to form even larger columns. The thin film growth process can thus be pictured as the manner in which cables are made for suspension bridges. Small cables are wound together to form larger cables, which are then wound together to form even large cables, etc. Messier has noted four different superstructures of this type in the
range of film sizes he has examined, and they are shown in Figure 2-5. An important feature of Messier's model is that the basic dendrites retain their identity, which explains the observations of Lissberger and Pearson. The forces that bind the dendrites and columns together are large, and it is difficult to see the basic structural units. Messier has developed a technique of lightly chemically etching his samples prior to examining them in order to bring out the detail of the microstructure. An example of the microstructure within the microstructure is shown in Figure 2-6 and in Figure 2-7, where the columnar structure within a nodule shows growth from a single starting point.

Summarizing, computer models have shown that the two most important factors in thin film growth are a limited mobility of condensing atoms or molecules together with self-shadowing of regions by atoms or molecules already condensed. Since vacuum deposition techniques enjoy widespread use for the manufacture of thin films, any improvement in the optical and mechanical properties of thin films should be based on modification of deposition conditions rather than upon radically new methods. As an example, the influence of substrate temperature upon film properties has been studied extensively. At higher substrate temperatures the resulting films are denser with a resulting increased durability.

Since higher substrate temperatures increase the mobility of the condensing atoms or molecules by adding energy, additional methods of increasing energy are likely candidates for closer examination.
Figure 2-5. Microstructure of columns.

(From Messier, 1982.)
Figure 2-6. Microstructure within microstructure.

(From Messier, 1982.)
Figure 2-7. Microstructure within module.

(From Messier, 1982.)
One of these methods, UV irradiation during deposition, is of particular interest because of studies of post-deposition UV irradiation and its effect upon film properties. Bradford et al. (1965) have irradiated SiO₂ films with quartz UV lamps and have noted two effects. First, the initial high absorptance of the films in the far UV has been essentially eliminated as shown in Figure 2-8. Second, the index of refraction of the films has been decreased by about 8% based upon measurements of the reflectance of the films at their interference minima. Bradford and his co-workers have attributed these effects to two entirely different processes. The first is a rearrangement of the oxygen atoms or molecules gettered during the deposition process and the formation of well defined silicon oxide molecules with low UV absorptance. The second is a further oxidation of the deposited film when the UV treatment is applied in air or oxygen.

Mickelsen (1968) has also studied the effects of post-deposition UV irradiation and noted the elimination of absorption in the 200- to 400-nm region. He has attributed this to the photorelease of electrons trapped at oxygen-ion vacancies, the trapped electrons being responsible for the UV absorption. In addition he has noted that UV-irradiated samples show greater stability of the dielectric constant with time than nonirradiated samples. This he attributes to a decrease in the migration of oxygen ions within the film.

Hodgkinson and Walker (1973) have studied the effect of post-deposition UV irradiation of SiO₂ but have concentrated on the change in mechanical properties. They have used the cantilever method of
Figure 2-8. Reduction of absorption due to post-deposition UV irradiation.

Effect of UV irradiation on the visible and UV reflectance of aluminum protected with 4100 Å of SiO. SiO evaporated at 9 x 10^{-5} torr of oxygen and deposited at a rate of 6 Å/sec. Irradiation performed with Hanovia lamp. (From Bradford et al., 1965.)
measuring stress by clamping one end of a film-coated substrate and measuring the deflection of the other end. When air has been admitted to the vacuum chamber, they have noted a large increase in the compressive stress. However, for samples irradiated by UV in a vacuum, they have noted a change from compressive stress to tensile stress, and after air has been allowed into the vacuum chamber, the stress again becomes compressive. Their explanation for this is that, prior to irradiation, the film has a loose structure with many oxygen molecules not bonded in the silicon oxide structure. The UV rearranges the oxygen molecules, producing well defined silicon oxide molecules and reducing the stress. Oxidation in an atmosphere, on the other hand, involves the addition of oxygen molecules to the film and an increase in compressive stress.

All of these studies show that UV irradiation has an impact on films already deposited. The influence of the UV irradiation should have a greater influence during the deposition process while columns are growing and before oxygen molecules are trapped. Another method of adding energy to the film growth process would be bombardment by either electrons or ions. Browning (1981) has studied the effect of bombarding growing films with electrons. Based on x-ray diffraction observations, he has found that for potassium hexafluorozirconate, electron bombardment during deposition eliminates crystal structure. On the other hand, he has found that electron bombardment has no effect on thin film growth of SiO. Because post-deposition electron bombardment shows no effect, he has concluded that the electrons are
not able to transfer energies to the molecules greater than the lattice bonding energies. This suggests that bombardment by ions heavier than the electrons might have a greater effect.

The use of ion bombardment is not a new area of study for the deposition of thin films. Hirsch and Varga (1980) have examined the improvement of film adherence by argon ion bombardment. Cuomo et al. (1982) have examined the modification of film stress by low-energy argon ion bombardment. Martin et al. (1983) were the first to investigate ion bombardment as a means of improving packing density. They have used ion bombardment of refractory oxide films and reported significant changes in packing densities of TiO₂ and ZrO₂. X-ray diffraction of the ZrO₂ films has shown that the ion bombardment promotes film growth in the face-center-cubic phase, while electron microscopy has revealed a disruption of columnar growth and an increase in surface roughness. Most significantly, they have found that narrow-band filters made during ion bombardment show an increased resistance to moisture penetration due to increased packing densities. In addition, there are many studies concerning sputtering that also involve ion bombardment and are thus of interest. These include Gautherin and Weissmantel (1978), Weissmantel et al. (1979), and Pawlewicz et al. (1982). Thus, ion bombardment also appears to be a way of influencing thin film growth.
CHAPTER 3

EXPERIMENTAL APPARATUS

High Vacuum Coating Plant

Because of the importance of controlling as many deposition parameters as possible, a state-of-the-art high vacuum coating plant was obtained for this research from the Balzers Company of Liechtenstein. The coating plant and its auxiliary equipment are collectively called the Balzers BAK 760 (Figures 3-1, 3-2, and 3-3). Putting the coating plant into operation and establishing the operating parameters was a time consuming process. Feedthroughs were added, support structures were installed, and procedures of operation were established. Calibration of the source materials and determination of the deposition conditions were critical to this research. For example, there is a tradeoff among oxygen pressures, substrate temperature, and deposition rates that determines the ideal conditions for the deposition of any one source material. As a result, a long series of test runs was necessary before any UV irradiation or ion bombardment could be attempted. Since this was the first project involving the use of the plant, points of operation needed to be detailed as a reference for future researchers. Rather than cover the operating details in this chapter, Appendix A has been included as an operating checklist. However, a description of the coating plant is included
Figure 3-1. Balzers BAK 760 high vacuum coating plant.

V = vacuum chamber; P = power supply;
L = UV lamp housing
Figure 3-2. Balzers BAK 760 power supplies and digital controller.
Figure 3-3. Interior of vacuum chamber.
here in order to document the conditions under which the thin films for this research were made.

The vacuum chamber itself is made of stainless steel and has a working area 888 mm wide, 923 mm high, and 950 mm deep. Tube coils are welded to the exterior walls and door to provide for heating and cooling of the vacuum chamber. A plate valve housing is attached to the rear of the chamber. A protective chevron is mounted in the opening between the working area and the valve housing to protect the valve plate from evaporants. Two large sight glasses are mounted in the door for visual monitoring of the coating process. Opening the door frees the entire cross section of the chamber, thus affording good accessibility to all internal equipment.

The roughing pump is a two-stage arrangement consisting of a Roots pump in series with a single-stage rotary vane pump with gas ballast (Balzers UNO 100). It is capable of reaching a pressure of $3 \times 10^{-2}$ mbar without gas ballast and a pressure of $5 \times 10^{-1}$ mbar with gas ballast. About 15 minutes is required for the roughing pump to rough down the chamber. High vacuum is obtained by a refrigerator cryo-pump (Balzers RKP 500), which uses liquid nitrogen. The advantage of using a cryo-pump is the elimination of an oil mist found when using a diffusion pump. The compressor unit is separated from the cryo-generator by means of flexible, high-pressure connecting lines in order to eliminate vibrations as much as possible. The cryo-pump is capable of obtaining pressures below $10^{-6}$ mbar. In practice, the cryo-pump is normally allowed to operate overnight in order to reach
this pressure. A pumping station control system (Balzers PC 101) is used to control the pumping and venting of the system. It monitors the pressure at various points in the system as well as the condition of the roughing pump and the cryo-pump. It automatically opens or closes the necessary valves by means of control signals. The pumping station control system also controls the flow of hot or cold water through the chamber wall tubes.

Pressure inside the chamber is monitored using an ionization vacuum gauge (Balzers IMG 060B). The pressure-dependent ion current of a hot-cathode gauge head is used for measurement. The electrons emitted from the cathode ionize the existing gas molecules on their way to the positive electron collector. The resultant positively charged ions are drawn off by an ion collector, and the measuring current is converted into a corresponding voltage by an electrometer amplifier which is displayed on the gauge. The emission current is held constant by a control circuit, and the ion current is proportional to the pressure within the measuring range. An alternative would have been a cold-cathode gauge, but these are not as accurate at very low pressures. Care must be taken not to operate hot-cathode gauges at too high a pressure, so a protection circuit is built into the ionization gauge control that automatically turns the filament of the gauge off at higher pressures. A manual switch is also provided for turning the filament on and off.

A regulating valve (Balzers RME 010) is mounted to the side of the coating chamber, and for this research was used to admit oxygen
at a controlled pressure during film deposition. A valve control unit (Balzers RVG 040) monitors a pressure-dependent electrical signal from the ionization gauge control and sends a control signal to the regulating valve. A precision potentiometer is used to select the desired pressure (called the "set point"), and a gauge on the control unit displays the valve voltage.

Four 2-kW quartz halogen lamps are mounted inside the coating chamber and used for heating substrates. The surfaces of the substrates to be coated are directly exposed to the radiant heat of the quartz lamps. This method of heating substrates is now becoming more popular than the old rear-surface type. The substrate temperature is preset on a control unit that controls two power controllers. Each controller supplies power to a pair of quartz lamps. The temperature inside the coating chamber is monitored using a thermocouple and is displayed on a digital unit. By comparing this temperature with the preset temperature, the control unit maintains the proper current for the quartz lamps. During this research, it was found that the location of the quartz lamps was critical for film deposition on a stationary substrate. The location of the lamps is shown in Figure 3-4.

Also shown in Figure 3-4 is the location of a glow discharge bar at the base of the coating chamber. This is the basis of a 700-W glow discharge system and is used as the final step in cleaning substrates. It will be covered in more detail under the topic of substrate preparation. Part of the glow discharge system is a regulating valve (Balzers RVE 016), which maintains the proper discharge current
Figure 3-4. Location of substrate heaters and glow discharge bar.

H = heater; B = bar
for the glow discharge by maintaining the proper gas pressure. Air is admitted to the coating chamber and maintained at a pressure of $4 \times 10^{-2}$ mbar. To control the rate at which the air is admitted, a throttling valve is built into the outlet end of the regulating valve. Although normally operated automatically, the throttling valve can be operated manually.

There are four evaporation sources mounted in the coating chamber; two of these use thermal heating and two use electron-beam heating (see Figure 3-5). In both cases, the thin film deposition process is called vacuum evaporation. An understanding of this evaporation process is necessary for understanding the formation of the microstructure of thin films. If a material is heated in air it will eventually vaporize, provided it does not decompose or react with its environment. The vapor is given off in a turbulent stream that is not uniform in time. When it strikes a cold surface and condenses, it produces a porous deposit that is generally not suitable for optical purposes. However, when the evaporation takes place in a vacuum, such is not the case. Most important, at sufficiently low pressures the evaporant will not react with the atmosphere. In addition, the vapor stream given off is even, and the evaporant molecules appear to travel in a straight line. If a cold substrate is properly prepared and inserted in the path of the evaporant, a useful film will be deposited (Macleod, 1969).

For vacuum evaporation, the first step necessary is the heating of the source material to change it from a condensed phase,
Figure 3-5. Location of thermal sources and electron beam sources.

(a) Right side view. T = thermal source; E = electron beam source
Figure 3-5—Continued

(b) Left side view. $T =$ thermal source; $E =$ electron beam source
either solid or liquid, to a gaseous state. The choice of heating method depends largely on the vaporization temperature of the source material. The most easily controlled method is thermal heating. In this method the source material is placed in a "boat" made of a refractory metal, such as tungsten, tantalum, or molybdenum. The boat serves the function of a crucible to contain the source material, and when an electric current is passed through it, it provides the heat necessary to vaporize the material. For this research, a tungsten coil was used to hold aluminum for deposition. Each thermal evaporation source has a 4-kVA high current transformer and is controlled by a digital system controller (Balzers BPU 100E), which will be discussed later. By use of the controller, the rate of deposition can be held constant.

Also in the coating chamber are two electron-bombardment-heated sources, more simply called electron-beam sources. Instead of being heated by resistance or induction heating, the source material is heated by an electron beam focused onto its surface. Most of the kinetic energy of the electrons is converted into heat, and higher evaporation temperatures can be reached. This is the biggest advantage to using electron-beam sources. Another advantage is that there is less interaction between the source material and its container. This is because the electron beam is focused onto the surface of the source material, and the portion of the source material in contact with the container is maintained at a lower temperature. Even materials that are very reactive, such as silicon which is hard to evaporate by any other method, can be used.
The two electron-beam guns (Balzers ESQ 310U) are designed for maximum flexibility. Three interchangeable crucibles can be selected, based on the number of materials needed for the film design and the amount of material needed. When two source materials are required in quantity, a large (80-cc), single-pocket, or pot, crucible is used. A crucible control unit (Balzers ETS 110) rotates the crucible to use the source material uniformly. A separate molybdenum liner is used for each source material, and placed inside the single-pocket crucible; this allows for easily changing source materials within one crucible. When many source materials are needed, a four-way crucible containing four separate 8-cc pockets is used. It is mounted with a crucible cap that exposes only one pocket at a time to the electron-beam gun. The crucible control unit is used to select which pocket is exposed. An oscillating crucible is similar to the four-way crucible except that two of the pockets are replaced by a 20-cc, crescent-shaped pocket that is oscillated during use. This crucible combines the advantage of a larger amount of one source material with the availability of several other source materials.

Each electron-beam gun has a separate 15-kW power supply (Balzers EHV 110A) and is controlled by a separate control unit (Balzers EKS 110A). The control unit provides power for the cathode in order to control the electron beam output and control the position of the beam spot on the evaporant. Electrons are produced by the heated cathode of the electron gun, extracted by an electric field potential, and focused by means of a voltage applied to a Wehnelt shutter. The electrons are deflected through approximately 270° by
means of a magnetic field, and strike the evaporant in the crucible. The y-sweep of the electron beam is controlled by a periodic variation of the deflection field, and the frequency can be adjusted from 2 to 40 Hz. The x-sweep of the electron beam is controlled by an additional electromagnetic field; the sweep frequency is 50 Hz. With a 10-kV acceleration voltage, the density of the electron beam at the crucible is 40 kW/cm². Since a very much lower density of 1 kW/cm² is needed for the evaporation of dielectrics, the beam is defocused by means of an electromagnetic AC field superimposed on the deflection field. A hand-held remote control allows for adjustment of the beam position, for fine control of the crucible position, and for remote switching off of the filament current. This is essential as a safety device since the beam can be controlled while the operator is looking at the source material in the crucible through the sight windows of the vacuum chamber door.

The electron-beam gun control unit can be operated either manually or automatically. The advantage of manual operation is that the power can be controlled while the operator is watching the material in the crucible. For automatic operation, it is necessary to determine both the power levels and the deposition rates that will be used. This must be done by making several trial runs under manual operation. The greatest advantage to automatic operation is that the deposition rate can be held constant more accurately than can be done manually. Another advantage is that a coating design can be repeated with coating parameters held as close to the same values as possible.
For automatic operation, the power supplies for the thermal evaporation sources and the electron gun control units are controlled by a microprocessor unit (Balzers QSR 101). This unit relies on information from a quartz crystal to accurately control film thicknesses and deposition rates. It also controls such auxiliary functions as shutter opening and closing, substrate rotation, and glow discharge. As shown in Figure 3-6, process parameters are entered through a keyboard, and can be displayed and updated at any time. For each of the four sources, the following information must be entered into the microprocessor: thickness of the layer in angstroms, deposition rate in angstroms per second, a material constant in grams per cubic centimeter which is proportional to the specific density of the coating material, four control times, and four power levels.

The control times and power levels are shown diagrammatically in Figure 3-7. The time T1 is the glow discharge time; time T2 is the recovery period after the glow discharge; time T3 is the rise time during which the power is increased from zero to power P1; and time T4 is the degassing time. The power settings are given as a percentage of the maximum power that can be achieved for a given source, and must be determined manually. Power P1 is the rise power and is the power level at which degassing begins. The degassing period is necessary to allow the source material to outgas and the system to return to the pressure required for deposition. Power P2, which may be higher or lower than power P1, is the degassing power and is the power reached at the end of time T4. Power P3 is the maximum power
Figure 3-6. Digital controller.

\( K = \text{keypad} \)
Figure 3-7. Control times and power levels.
that can ever be applied for a given source, and is selected for safety reasons. Finally, power P4 is a holding power that maintains the source material at a temperature below the vaporization temperature. Typical values for these parameters as used during this research are given in Appendix B.

The quartz crystal is mounted in a water-cooled copper shield in the vacuum chamber just below a rotating substrate holder. As material is being evaporated, it condenses on an exposed portion of the quartz crystal just as it condenses on the substrate. The frequency of the quartz crystal changes from its natural frequency owing to the additional mass, and the change of frequency is given by

$$\frac{df}{f} = -\frac{m}{\rho Ad}$$

where \( f \) is the natural frequency, \( d \) is the thickness of the quartz, \( \rho \) is the density of the quartz, \( A \) is the area of the quartz, and \( m \) is the mass covering the quartz. The thickness of the coated layer is then given by

$$th = \frac{K}{\rho'} \left( \frac{1}{f} - \frac{1}{f_o} \right)$$

where \( th \) is the thickness of the layer, \( \rho' \) is the density of the coating material, \( f_o \) is the starting frequency, \( f \) is the measured frequency, and \( K \) is a constant. In the microprocessor, the value \( M \) is used to input the constant for this equation.

The actual frequency change of the quartz crystal not only depends on the mass of the material being deposited, but is affected by temperature stability and the kind of holder used for the crystal.
In this case, the crystal holder is water cooled to assure a high temperature stability of the quartz. The holder is also designed to put a minimum amount of mechanical pressure on the quartz so as not to distort the frequency.

To calibrate the material constant for each material, the thickness of a layer being deposited must be determined by a means additional to the quartz crystal. For this reason, and for manual operation, an optical thin film monitoring system (Balzers GSM 210) is used. The components of the optical monitoring system are shown in Figure 3-8. A light source, powered by a stabilized voltage source, produces a light beam that is modulated or chopped at 80 Hz by a rotating chopper blade. The light beam enters through a window in the base of the vacuum chamber and strikes a monitor plate positioned in the plane of the substrates to be coated. For this research the monitor plateholding assembly was modified to hold a stationary substrate, so that the substrate itself acts as a monitoring plate. The modulated light that is reflected from or transmitted through the substrate is detected by separate four-stage blue photomultipliers, whose spectral sensitivity is shown in Figure 3-9. An alternating current proportional to the light intensity is then sent to a monitoring instrument that displays both the amount of total light and the percentage of reflection or transmission. To ensure that light from the evaporation sources, substrate heaters, room lights, etc., is not included in the measurements, the amplifier in the monitoring instrument is selectively matched to the modulation frequency. A filter
Figure 3-8. Optical monitoring system.

A  Light source
B, C  Photomultiplier tubes
D  Monitoring instrument
E  Monitor plateholder
Figure 3-9. Spectral sensitivity of photomultiplier tube.
holder is mounted in the photomultiplier tube assembly, and a pair of interference filters is used to select the monitoring wavelength. The spectral transmission of the pair of filters is shown in Figure 3-10.

**Ultraviolet Source**

A 1000-W mercury-xenon lamp was used as a UV source for this research. As shown in Figure 3-11, the lamp house (Kratos LH151) was mounted on the side of the coating chamber. Although it would be desirable to mount the UV source under the coating chamber so that the beam of light could be directly aimed at the substrates, space limitations under the coating chamber prevented this choice. The walls of the lamp house are of heavy duty construction as a safety precaution in the event the arc lamp explodes. The lamp housing has an internal blower to provide cooling ventilation for the lamp. However, as an additional safety measure, an external blower system was connected to the output vent to remove ozone from the laboratory area. The condensing system of the lamp house uses 3.81 cm (1-1/2 in.) optics with an f-number of 1.5.

A mercury-xenon lamp was chosen in preference to pure mercury because it should have a longer life and be more stable in use. However, xenon has the disadvantage of a high output in the near infrared. Figure 3-12 shows the spectral output of the mercury-xenon lamp. To limit the purely thermal effects of the long-wavelength light, a Schott UC-5 spectral filter was used to filter out the visible and infrared portions of the spectrum. The spectral transmission of this filter is shown in Figure 3-13. The light from the lamp
Figure 3-10. Spectral transmission of monitoring filters.

Expanded plot of peak region is shown at upper left.
Figure 3-11. UV lamp house and power supply.
Figure 3-12. Spectral output of mercury-xenon lamp.
Figure 3-13. Spectral transmission of UG-5 filter.
is transmitted into the vacuum chamber through a sapphire window, chosen because of its high ultraviolet transmittance, and onto a mask with a slit. Then the light is directed onto the stationary substrate by means of two aluminized folding mirrors. The components of the UV system are shown in Figure 3-14.

The amount of UV radiation reaching the samples should be enough to increase the mobility slightly. The energy of a UV photon is on the order of the bonding energy of the material, and it is necessary to ensure a photon arrival rate comparable to the material arrival rate. For the UV system selected for this research, it was difficult to calculate this rate because of losses in transmission through the sapphire window of the vacuum chamber and the losses due to reflection from the two mirrors. However, a measurement of the UV irradiation reaching the sample was made using a Coherent Model 210 Power Meter.

With the Schott UG-5 filter present in the system, a power of 0.5 W or J/s was measured at the substrate location. The energy of each photon was calculated using the simple equation

$$E = h \frac{c}{\lambda}$$

where the wavelength $\lambda$ is some average wavelength within the UV region. For a value of $3 \times 10^{-7}$ m, the result was $6.62 \times 10^{-19}$ J/photon. Thus, the rate at which photons arrive at the substrate is $7.5 \times 10^{17}$ per second.
Figure 3-14. Schematic of UV system.
The rate at which source material arrives at the substrate depends on the deposition rate selected for that material. As a representative number, a quarter wave of SiO₂ takes 1 minute to deposit. At a monitoring wavelength of 500 nm, a quarter wave has a thickness of $1.25 \times 10^{-7}$ m. Multiplying Avogadro's number by an SiO₂ density of $5.9 \times 10^6$ g/m³, there are $6.34 \times 10^{28}$ molecules/m³. For a sample size of $2.25 \times 10^{-4}$ m², a volume of $2.81 \times 10^{-11}$ m³ is deposited in 60 seconds; this yields a material arrival rate of $2.97 \times 10^{16}$ molecules per second. Comparing the two rates just calculated, there should be 25 photons per arriving molecule, a more than adequate ratio.

As an additional UV source, a 160-W mercury lamp (General Electric HSB160/PS30/M) can be mounted inside the vacuum chamber. The outer glass bulb was removed, and four electrical wires were connected to the lamp. Two of the wires were connected to the high voltage lead-throughs normally used for an ion gun. These lead-throughs were in turn connected to the 120-V line voltage in the laboratory. The remaining two lead-throughs were connected to two of the pins of a seven-pin lead-through mounted on the side of the vacuum chamber, and used to start the lamp. No ballast was required for this lamp. In this paper, the lamp is referred to as the interior UV source.

**Ion Source**

A water-cooled inverted magnetron ion gun (Figure 3-15) is used as an ion source. The ion gun is so called from its discharge
Figure 3-15. Inverted magnetron ion gun.

G = ion gun
geometry, and is capable of producing a well focused intense beam of ions. It is a cold-cathode, magnetically enhanced discharge source, in which ions are extracted through an aperture in the cathode wall. After extraction, the ion beam is collimated and focused by a system of electrodes. A single extraction aperture of 3 mm diameter is used. The voltage applied between anode and cathode is called the discharge voltage, and the voltage applied to the electrodes for extraction and focusing is called the beam voltage. Both argon and oxygen ions were used for this research. Calibration values for different discharge voltages and beam voltages are given in Table 3-1. A more detailed description of the geometry and operation of the ion gun is given in Appendix C.

Substrate Preparation

The substrates used for this research were either 1- x 3-inch glass microscope slides or 1- x 1-inch fused quartz samples. In both cases, the substrates were cleaned following the same procedure. First, the substrates were immersed in warm chromic acid for about 30 minutes. They were then drained, rinsed, and scrubbed by cotton using liquinox soap and deionized water. They were then rinsed using deionized water, and placed in an ultrasonic bath of deionized water and liquinox for about 20 minutes. After this they were placed in an intermediate ultrasonic rinse of deionized water, followed by a final ultrasonic rinse at a different frequency in deionized water. Finally, they were blown dry with nitrogen from an electrostatic nozzle gun. The cleaning procedure is designed to remove surface contamination.
Table 3-1. Calibration of Ion Gun

<table>
<thead>
<tr>
<th>Discharge current (mA)</th>
<th>Discharge voltage (V)</th>
<th>Beam current (mA)</th>
<th>Beam voltage (V)</th>
<th>Measured output (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Argon ions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>400</td>
<td>2.3</td>
<td>1200</td>
<td>24</td>
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<td>12</td>
<td>400</td>
<td>2.5</td>
<td>1200</td>
<td>28</td>
</tr>
<tr>
<td>12</td>
<td>400</td>
<td>*</td>
<td>1800</td>
<td>*</td>
</tr>
<tr>
<td>14</td>
<td>400</td>
<td>0.2</td>
<td>2200</td>
<td>60</td>
</tr>
<tr>
<td>16</td>
<td>400</td>
<td>0.4</td>
<td>1500</td>
<td>51.9</td>
</tr>
<tr>
<td><strong>Oxygen ions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>0.2</td>
<td>1500</td>
<td>30.2</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>0.2</td>
<td>2000</td>
<td>45.5</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>0.2</td>
<td>2500</td>
<td>43.0</td>
</tr>
<tr>
<td>15</td>
<td>400</td>
<td>0.35</td>
<td>1500</td>
<td>35.6</td>
</tr>
<tr>
<td>15</td>
<td>400</td>
<td>0.2</td>
<td>2000</td>
<td>77.7</td>
</tr>
<tr>
<td>20</td>
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<td>0.5</td>
<td>1000</td>
<td>16.6</td>
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<tr>
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<td>0.4</td>
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<td>0.25</td>
<td>1800</td>
<td>73.1</td>
</tr>
<tr>
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<td>400</td>
<td>0.2</td>
<td>2000</td>
<td>95.6</td>
</tr>
<tr>
<td>20</td>
<td>400</td>
<td>0.2</td>
<td>2500</td>
<td>103.5</td>
</tr>
</tbody>
</table>

Note: All readings taken with a pressure of $1 \times 10^{-5}$ mbar.

*Discharge breaks down.
since such contamination decidedly influences thin film growth and adhesion. The final cleaning process is glow discharge cleaning and is accomplished in situ immediately prior to thin film deposition. A detailed description of substrate cleaning, including glow discharge cleaning, is given by Maissel and Glang (1970) and will not be included here.

**Source Materials**

Two materials with high index of refraction were used for this research: titanium oxide (Ti$_2$O$_3$) in the form of 1/4-in. to 1/8-in. pieces of 99.9% chemical purity from Cerac, and zirconium oxide (ZrO$_2$) tablets from E. Merck Chemicals. Silicon oxide (SiO$_2$), in the form of 1/2-in. to 1/8-in. fused pieces of 99.99% chemical purity from Cerac, was used as a low index material. The materials chosen for examination are the most commonly used dielectric materials in thin film work, and improvements in their deposition would be of the greatest interest.

The Ti$_2$O$_3$ is a better source material for the production of TiO$_2$ than just simply using TiO$_2$. TiO$_2$ loses oxygen on heating, and this is the reason for requiring reactive evaporation. In addition, the TiO$_2$ within the crucible gradually changes in composition toward lower oxides as film layers are being deposited. Thus, to ensure stability of the composition of the source material, it is preferable to use Ti$_2$O$_3$ (Pulker, Paesold, and Ritter, 1976). Even with this material, higher oxygen pressures are required in the vacuum chamber than are required for ZrO$_2$. Also, it has been found that powdered forms of
SiO$_2$ cannot be used in the Balzers BAK 760 because of the speed with which the roughing pump evacuates the coating chamber; the result is to "blow" the powder out of its crucible. The small pieces of SiO$_2$ described have not suffered from the same problem.
CHAPTER 4

METHODS OF ANALYSIS

To detect any macroscopic or microscopic changes in films that have been irradiated with UV and/or bombarded with ions, a number of methods of analysis are used. Each method is described in its own section below.

Dektak Profilometer

For measurements of physical thickness, a Sloan Dektak Surface Profile Measuring System is used. It is capable of measuring surface profiles from less than 2.5 nm to a maximum of 100,000 nm. In operation, a sample is placed on a stage located beneath a sensing head. The sensing head contains a diamond stylus with a tracking force of about 50 mg. As the sensing head moves relative to the sample, height information is recorded on a strip chart. For measurements of film thickness, a mask should be used during the preparation of the film so that an uncoated portion of the substrate can be used as a reference height.

Spectrophotometer Analysis

Since thin films are used to modify the optical properties of surfaces, optical techniques are useful in analyzing thin films. A spectrophotometer is a device that measures either reflectance from or transmittance through a sample as a function of wavelength over a
wide spectral range. This information can then be used to compute the optical constants of the film(s).

The Cary Model 14 spectrophotometer measures reflectance and transmittance by comparing the relative intensities of two different beams from the same optical source. The two beams are generated by a rotating semicircular mirror that chops the beam at 30 Hz, alternately sending half of the beam to the sample and using the other half as a reference. An optical diagram of the system is given in Figure 4-1. A tungsten lamp acts as a source for the portion of the visible spectrum between 300 and 650 nm; a deuterium lamp is the source for the portion of the UV spectrum from 200 to 300 nm. The wavelength of the incident light is scanned using a 30° fused silica prism in series with a 600-line/mm grating, each with its own collimating mirrors and slit system. Because the pulses of light of the reference beam and sample beam are out of phase with each other, a single photomultiplier tube is used to detect the light. To correct for variations between the output of the source and the responsivity of the photomultiplier tube, a bank of compensating resistors is used.

Before reflectance or transmittance data are taken, a 100% line is established by comparing the reference and sample beams with no sample present. The balance between the two beams must be re-adjusted each time the instrument is changed from reflectance to transmittance and vice versa. In addition, the balance must be adjusted when a new sample holder is used. After the beams have been balanced so as to give a reading of 100%, the sample is positioned in
Figure 4-1. Optical diagram of Cary 14 spectrophotometer.
the sample beam and the wavelength scan is repeated. The reflectance and transmittance data can then be used to determine the optical constants of the film(s).

When a thin layer of material of index of refraction $n_m$ is deposited on a substrate of index $n_s$, the electric and magnetic fields change as a beam of light travels from one surface to the next. Optical admittance is defined as the ratio of the magnitudes of the magnetic and electric fields, and the change of optical admittance during propagation from one surface to the next can be found by using the characteristic matrix for a film layer in the equation

$$
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
\cos\delta & \frac{i \sin\delta}{n_m} \\
i n_m \sin\delta & \cos\delta
\end{bmatrix} \begin{bmatrix}
1 \\
n_s
\end{bmatrix}
$$

where $B$ is the electric field strength, $C$ is the magnetic field strength, $d$ is the geometrical layer thickness, and $\delta$ is the phase. The phase is calculated using the equation

$$
\delta = \frac{2\pi d}{\lambda} n_m
$$

where $\lambda$ is the wavelength of the light.

For the case of lossless layers whose optical thickness is an integer multiple of a quarter wavelength, the phase reduces to an integer multiple of $\pi/2$. The characteristic matrix then reduces to
for an odd number of quarter waves, and
\[
\begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}
\]
for an even number of quarter waves. The result is that the effective admittance for an odd number of quarter waves is given by the simple relationship
\[
n_f = \frac{n_m^2}{n_s}
\]
and for an even number of quarter waves, i.e., half waves, the layer acts as though it were not there.

The reflectance from a surface is given by a form of the Fresnel equations, and for a substrate/film assembly whose effective index is \(n_f\) the relationship is
\[
R = \frac{(1 - n_f)^2}{(1 + n_f)^2}.
\]
Since any odd number of quarter waves can be treated as one quarter wave plus a number of absentee layers, the reflectance of a substrate/film assembly will cycle between the reflectance from the bare substrate to the reflectance of one quarter wave deposited upon the substrate. Figure 4-2 is a plot of transmittance versus thickness, and if the deposition rate is held constant, a plot of transmittance versus time will look the same.
Figure 4-2. Plot of transmittance versus thickness of thin film.
The preceding discussion was in terms of a single monitoring wavelength. However, there will be multiple wavelengths for which a film layer looks like either a quarter wave or a half wave. Using Figure 4-3, it can be seen that the equation for the index of refraction of a film is

\[ n_f = \frac{m \lambda}{2d}, \]

where \( d \) is the physical thickness and \( \lambda \) is the wavelength at which transmittance is an extremum. For a film whose index of refraction is higher than the substrate index, this will be a minimum; for a film with a lower index than the index of the substrate, it will be a maximum. A single measure of transmittance at one wavelength will not yield both thickness and index information. Either a physical measurement of thickness must be made, or multiple measurements of transmittance must be taken at various wavelengths.

To this point, the absorption is assumed to be zero and reflectance and transmittance will sum to 1. However, if absorption is present, then the sum of reflectance and transmittance will be less than 1; the difference between unity and this sum represents the absorption or film losses. This is a rough approximation since it does not take into account losses from the substrate itself. However, it gives a quantitative measure of absorption and is an improvement of the qualitative measure found by holding the film up to the light and seeing how "dark" it is.
Figure 4-3. Plot of transmittance versus wavelength of thin film.

Upper curve, the reference curve, represents 100% transmittance. Lower two curves are samples.
Since there are many combinations of film thickness and film index that yield the same phase thickness for a film, a computer program can be used to sort out which values are correct. Such a computer program has been written by Dr. Bill Case of the Vought Corporation, Dallas, Texas. The inputs are transmittance, front surface reflectance, and rear surface reflectance for a single wavelength. It is assumed that the index of refraction of the substrate is known. The output gives combinations of physical thickness and optical constants, using a merit function to indicate the closest values.

Narrowband filters can also be examined using the reflectance and transmittance curves from a spectrophotometer. The simplest narrowband filter is a Fabry-Perot etalon, that is, two reflecting surfaces located a distance d apart. The phase thickness of the etalon is given by

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

where n is the index of the spacer and \( \theta \) is the tilt angle. For the case of equally reflecting surfaces and phase shifts upon reflection of 0° or 180°, the transmittance of the filter is given by

$$T_F = \left( \frac{T}{(1 - R)^2} \right) \left( \frac{1}{1 + F \sin 2\delta} \right)$$

where

$$F = \frac{4R}{(1 - R)^2} ,$$

which produces a set of narrow transmission bands centered where the
phase is an integer number times $\pi$. The width of the pass band measured at half the peak transmittance is given by

$$\Delta\lambda_H = \frac{1 - R}{m\pi\sqrt{R}} \cdot \lambda_p$$

where $\lambda_p$ is the peak wavelength. The resolving power of the etalon is the product of the order number and the finesse, where the finesse is given by

$$\mathcal{R} = \frac{\pi\sqrt{R}}{1 - R}.$$

The all-dielectric equivalent of the etalon consists of a spacer layer whose thickness is a multiple number of half waves with a quarter-wave stack on each side to act as the reflectors. With an all-dielectric narrowband filter it is possible to achieve halfwidths in the visible of 0.5 nm with peak transmittance exceeding 50%. Since the peak transmission wavelength depends on the index of refraction of the spacer layer, narrowband filters are a sensitive measure of a shift in the index.

**FECO Interferometer**

Two problems were encountered with the use of the spectrophotometer during the course of this research. First is the amount of time it takes to run a trace of a narrowband filter. Because of the rapid penetration of moisture into thin films, the peak wavelength of the filter shifts during the course of a measurement. Second, a number of narrowband filters have been bombarded with ions, and the bombarded region is circular with a diameter of only a centimeter.
Because the region is so small, it is difficult to close down the height of the slits of the spectrophotometer to match the sample area.

For this research, a FECO interferometer was modified in order to quickly examine the peak wavelength of a very small region of a narrowband filter. The normal use of this type of interferometer is to examine surface topology by looking at bright fringes of equal chromatic order (FECO). For this research, a silvered mirror that would normally be present was removed and the narrowband filter was illuminated with a white-light source. The reflected spectrum from the filter was then examined using the remainder of the FECO apparatus. Since a narrowband filter is made to transmit a very narrow band of light, the reflectance spectrum will look like the output of the white-light source minus a very narrow band. In fact, if the area under examination has regions with different peak wavelengths, then the dark fringe will follow a line corresponding to the same optical thickness. As a result of this, it is possible to watch the adsorption of moisture into a filter as the progression of a “spike” growing in the dark fringe, the peak of the “spike” corresponding to the maximum change of effective index of refraction as the moisture penetrates. In addition, if there is birefringence in the narrowband filter, then a polarizer can be placed over the illuminating white light source and the peak wavelength for both transverse-electric and transverse-magnetic polarizations can be examined. It should be emphasized that although the term FECO interferometer is used in this paper for this
experimental setup, the device is not operated as a true FEO interferometer.

**Adhesion, Hardness, and Durability**

On a macroscopic level, the physical properties of interest for a thin film are the adhesion of the film to the substrate, the hardness of the film, and the durability of the film, in particular the resistance to moisture adsorption. A few simple tests of these properties were performed on samples that had been UV irradiated and ion bombarded. More sophisticated devices exist for the measurement of surface hardness, but none were available.

The test used to measure adhesion between a film and substrate is called the "Scotch tape" test. As the name suggests, a piece of household cellophane tape is applied to the film and then pulled off. The degree to which the film is removed from the substrate is an indication of adhesion. Every attempt was made to apply the cellophane tape with the same amount of force each time.

To measure surface hardness, an equally simple "eraser" test was performed on the samples. For this test, a pencil eraser is rubbed repeatedly over a spot on the sample to see how susceptible the film is to scratching. The amount of damage to the film is an indication of how well the film holds together. Again, every attempt was made to apply the same number of eraser strokes with the same amount of force to all samples.

A Blue M Company Model VP 100AT-1 humidity chamber was used to measure the resistance of films to moisture penetration. Samples
placed in the humidity chamber were subjected to a high humidity for more than 48 hours. The relative humidity was held constant and determined by the readings of both wet and dry bulb thermometers. A relative humidity of 97% was calculated for a dry bulb temperature of 40°C and a wet bulb reading of 39.5°C. It should be mentioned that, during the course of the research of Lee (1983), he and the author made a number of narrowband filters, some of which were irradiated with UV. Lee performed a series of calibrated exposures to different relative humidities but noted no differences for irradiated and non-irradiated samples.

**X-Ray Diffraction**

On the microscopic level, x-ray diffraction techniques are used to determine the crystalline structure of materials. This is true whether the material is in bulk form or in thin film form. The theory of x-ray diffraction began in 1913 when W. L. Bragg found that crystalline substances gave characteristic patterns of reflected x-radiation. For certain sharply defined wavelengths and directions of incidence, intense peaks of scattered radiation are observed. These peaks are now called Bragg peaks. The theory of x-ray diffraction is covered by many authors, among them Cullity (1956) and Ashcroft and Mermin (1976), and only a brief summary is included here. The x-ray diffraction techniques have been used before to determine the preferential orientation of evaporated thin films (Coleman, Turner, and Ullrich, 1947).
A Norelco Type 12045 x-ray diffraction unit was used to generate x-rays, and a Hewlett-Packard 7047A X-Y recorder was used to record the x-ray diffraction pattern of the samples. This device produces Cu-Kα x-rays from a copper source tube; the wavelength of this radiation is 0.154178 nm. The voltage of the source is set to 30.5 kV. A beam of x-rays is defined by a narrow 1° slit, and strikes the sample at some incident angle θ. Although the samples scatter x-rays in all directions, the detector is positioned so as to receive only those x-rays scattered at the same angle θ relative to the sample. This is an angle of 2θ relative to the incident beam. A filter within the detector is used to block secondary x-ray emissions at longer wavelengths. Figure 4-4 is a diagram of this process.

The diffraction process begins with the scattering of x-rays in all directions from each atom of the sample material. For a crystalline structure, the atoms form a regular periodic structure and the scattered x-rays interfere with each other to form a pattern. For the rays to interfere constructively, the well known Bragg condition must be met. This is given by the equation

\[ m\lambda = 2d \sin \theta \]

where \( m \) is an integer, \( \lambda \) is the wavelength, \( \theta \) is the angle of incidence, and \( d \) is the spacing between parallel planes within the lattice. The strongly scattered Bragg peak is scattered at the same angle as the incident beam. Thin films can be composed of many planes of crystalline structure, and whenever the x-rays strike a particular set of lattice planes at the Bragg angle, a strong diffraction
Figure 4-4. X-ray diffractometer diagram.
peak is noted. Each peak in the x-ray diffraction pattern corresponds to a particular set of lattice planes. If the x-ray wavelength is known, then the plane spacing d can be computed for a given angle \( \theta \). A table of interplanar spacing has been compiled by Fang and Bloss (1966) and is given as a function of \( 2\theta \) for a variety of x-ray sources. Tables are available that list the lattice spacings and relative strengths of the diffraction peaks for a number of materials. Also given in the tables are the Miller indices, which describe how the atoms within a crystalline structure are arranged in a unit cell.

For materials that do not have a crystalline structure, i.e., amorphous materials, the x-ray diffraction profile will show no obvious peaks and will consist largely of noise. For a multilayer thin film assembly, the layers of amorphous material will not show up on the x-ray diffraction trace, but an x-ray diffraction analysis can be made of the remaining layers. Also, x-ray diffraction profiles have been run on the source materials as they exist before deposition. To prepare these samples, the source materials are first reduced to powder, then attached to a substrate by means of double-sided cellophane tape.

Transmission Electron Microscope

While x-ray diffraction data show the internal crystalline structure of films, they cannot reveal the columnar structure normally related to thin film growth. However, Pearson (1970) and Guenther and Pulker (1976) have shown that carbon replicas of thin film structures can be examined using a transmission electron
microscope. The carbon replicas are prepared following the procedure described by Pearson.

First, a diamond tip is used to score the coated side of a substrate. If firm pressure is applied to the opposite side of the substrate, it will break along a clean line that begins at the inscribed scratch. A cross-sectional view of the substrate and thin film coating is then exposed. The sample is then placed in a small vacuum chamber, with the edge exposed to two source materials. The edge is first coated with a platinum-carbon preshadow at an angle of about 70°; it is then coated with a layer of pure carbon deposited at an angle of about 45°.

After the sample is removed from the vacuum chamber, the carbon film is divided into small sections by scoring with a diamond tip. The sample is then dipped into a 5% solution of hydrofluoric acid, and the carbon film floats free. During this procedure care must be taken to ensure that the carbon film does not break apart along the corner of the edge formed by the top of the film and its cross section. To dissolve away any traces of the original film material, the sample is left in the acid solution for a period of about 12 hours. The acid solution is then replaced by deionized water and the carbon film is broken up into the small sections previously scribed. The sections are removed by lifting them out of the deionized water with 300-mesh copper grids. These grids serve as a support structure for viewing the replicas in a transmission electron microscope.
CHAPTER 5

RESULTS

A number of narrowband filters of either 17 or 21 layers and a number of single-layer coatings were made for this research. A list of these thin film coatings and the deposition conditions under which they were made is included in Appendix D. The analysis of these samples, which includes both UV irradiation experiments and ion bombardment experiments, will be discussed by method of analysis.

X-Ray Diffraction

As a reference point, the source materials used in this research were ground into powder and examined using the x-ray diffraction apparatus. A sample of the substrate used to hold these powders was also examined to ensure that the substrate itself would not contribute to the diffraction peaks. The SiO$_2$ source material is itself amorphous, as shown in Figure 5-1. The ZrO$_2$ source material (Figure 5-2) has strong diffraction peaks, in agreement with the peaks identified by Sanders, Farabaugh, and Haller (1982). The Ti$_2$O$_3$ source material (Figure 5-3) also has strong diffraction peaks, which correctly identify it as Ti$_2$O$_3$.

An analysis of single-layer samples indicated that SiO$_2$ remains in amorphous form when deposited. This is in agreement with the results of others (Browning, 1983). The application of both UV
Figure 5-1. X-ray diffraction pattern of powdered SiO$_2$ source material.
Figure 5-2. X-ray diffraction pattern of powdered ZrO$_2$ source material.
Figure 5-3. X-ray diffraction pattern of powdered Ti$_2$O$_3$ source material.
and ion bombardment does not change this amorphous structure; that is, it remains amorphous.

For single-layer samples of ZrO₂, a sample deposited with neither UV irradiation nor ion bombardment has shown that this material has a strong tendency to remain polycrystalline; although low temperature monoclinic peaks disappear, a single tetragonal peak (111) remains at about 30°. This is in agreement with the findings of Sanders et al. (1982), who have studied the effect of substrate temperature on evaporated ZrO₂. As shown in Figure 5-4, the addition of UV irradiation has little effect on this structure. The effect of ion bombardment (Figure 5-5) is to enhance the tetragonal peak, indicating that the ion bombardment process has increased the crystalline order of the sample.

In the case of TiO₂ films, all single-layer samples seem to indicate an amorphous structure since there are no apparent peaks in the diffraction patterns. However, another reason for the absence of diffraction peaks could be that the single-layer samples are too thin for x-ray diffraction purposes. Pawlewicz, Exarhos, and Conaway (1983) have stated that it is difficult to characterize TiO₂ films that are thinner than 150 nm or that are amorphous. They have successfully used Raman spectroscopy to characterize such films, but such equipment was not available for this research. However, since it has been found that SiO₂ films are amorphous, it is possible to use narrowband filters made of SiO₂ and TiO₂ to determine the crystalline structure of the TiO₂.
Figure 5-4. X-ray diffraction pattern of single-layer ZrO$_2$ sample: effect of UV irradiation.

(a) Nonirradiated. (b) UV irradiated.
Figure 5-5. X-ray diffraction pattern of single-layer ZrO₂ sample: effect of ion bombardment.

(a) Nonbombarded. (b) Ion bombarded.
An analysis of UV irradiated SiO₂/TiO₂ filters reveals diffraction peaks for the region of the filter not irradiated with UV (Figure 5-6a). There is a strong diffraction peak at a 2θ value of 25.3°, with additional peaks at 38° and 48°. These diffraction peaks are characteristic of the anatase form of TiO₂, and this is in agreement with the results of Pawlewicz et al., whose Raman techniques have also revealed the anatase form. For the region of the filter irradiated with UV, the strength of these peaks is reduced (Figure 5-6b). This result is significant because it indicates that the UV is capable of reducing the crystalline order of this material, tending toward amorphous structures.

If the samples just mentioned are rotated 90° in the x-ray diffraction sample holder, the results are as shown in Figures 5-6c and 5-6d. For the sample that was not irradiated with UV, the strength of the diffraction peaks is reduced in much the same way as it is reduced if irradiated with UV. For the sample that was irradiated with UV, the effect of rotation of the samples is to reduce the peaks even more until the sample appears almost amorphous. There are two possible explanations for this anisotropy.

The first explanation involves the columnar structure with which thin films grow as a result of limited mobility and self-shadowing. The maximum degree of shadowing is in a plane defined by the vapor incidence and the normal to the substrate. In a second plane perpendicular to the first, the shadowing is less. This is illustrated in Figure 5-7. The result is that oblique incidence
Figure 5-6. X-ray diffraction pattern of Ti$_2$O$_3$/SiO$_2$ narrowband filter: effects of UV irradiation and rotation.

(a) Nonirradiated. (b) UV irradiated.
Figure 5-6--Continued

(c) Nonirradiated, rotated 90°.
(d) UV irradiated, rotated 90°.
Figure 5-7. Anisotropy of growing films.
deposition often results in a change in column shape. If a cross section is taken of a column that has been normally deposited, it appears circular. However, a cross section of films that are deposited at oblique incidence yields columns that are elongated in the direction perpendicular to the vapor incidence and the normal to the substrate. This result has been verified by micrographs made by Leamy et al. (1980), who have noted that the resulting voids are also elliptical.

For x-rays striking the film/substrate assembly in a plane along the longest axis of the ellipse, the crystalline order extends over a greater length, and hence there is a stronger diffraction peak. When the sample is rotated 90°, the x-rays strike the sample along the shorter axis of the ellipse. For the UV irradiated portion of the sample, the crystalline order is very low and the corresponding diffraction peaks are small. When the sample is rotated 90°, the crystalline order along this direction is so low that diffraction peaks are difficult to detect.

A second possible explanation depends upon the nature of Bragg reflection. Although it has been stated that Bragg reflection occurs for planes parallel to the substrate, the actual reflection occurs for planes that are parallel or almost parallel to the substrate. This is one reason that x-ray diffraction peaks are lines that have some spread to them. In fact, one method of obtaining better diffraction peaks is to "rock" the sample while it is being examined with x-rays. Such an attachment was not available for the x-ray diffractometer
used for this research. Thus, there is a possibility that the planes responsible for the diffraction peaks are nearly parallel to the substrate and produce strong peaks in one direction and weaker peaks in the other direction.

For ion bombarded samples of SiO₂/TiO₂ filters, no diffraction peaks were seen (Figure 5-8). This was true for any region of the filter examined, and appears to indicate that even small amounts of ion bombardment are capable of reducing the crystalline order of TiO₂. Pawlewicz (1983) has found that TiO₂ is amorphous when deposited by RF sputtering on substrates that have a bias voltage of just 300 V, indicating that relatively small increases in mobility cause this material to become amorphous when deposited.

Spectrophotometer Analysis for Narrowband Filters

As indicated in Chapter 4, narrowband filters are a sensitive diagnostic tool since the peak wavelength of the filter is very sensitive to changes in refractive index. Additional information, such as the amount of absorption in the film, can also be found in the spectrophotometer traces of these filters. The fact that this is indeed a sensitive tool can be seen by examining Figures 5-9, 5-10, and 5-11.

Each of these traces is of a ZrO₂/SiO₂ filter deposited with the interior UV source irradiating part of the filter. Looking at the peak of the filter for both the irradiated and nonirradiated regions in Figure 5-9, it can be seen that the absorption is the same for both regions. The shift of peak wavelength to the right indicates that the spacer layer is either thicker or has a higher index of refraction. In
Figure 5-8. X-ray diffraction pattern of Ti$_2$O$_3$/SiO$_2$ narrowband filter: effect of ion bombardment.

(a) Nonbombarded. (b) Ion bombarded.
Figure 5-9. Spectrophotometer trace, sample 105.

Upper curve, the reference curve, represents 100% transmittance. The two lower curves represent different locations on the sample, one UV-irradiated (UV) and the other nonirradiated.
Figure 5-10. Spectrophotometer trace, sample 106.

The two curves represent different locations on the sample, one UV-irradiated (UV) and the other nonirradiated.
Figure 5-11. Spectrophotometer trace, sample 108.

Upper curve, the reference curve, represents 100% transmittance. The two lower curves represent different locations on the sample, one UV-irradiated (UV) and the other nonirradiated.
both Figures 5-10 and 5-11, the nonirradiated region shows more absorption. Thus in two out of three cases, the UV irradiation improves the transmittance of the peak wavelength, and in no case is it worse.

The effect of UV irradiation upon the absorption within TiO$_2$/SiO$_2$ filters is not clear. Although some samples indicated an improvement in absorption, others indicated increased absorption. However, it has been noted that there is an improvement in stability of the UV irradiated portions of these filters. Figure 5-12 shows the effect of baking a TiO$_2$/SiO$_2$ filter at 125°C for more than 72 hours, then watching the behavior of the filter as moisture repenetrates. The UV irradiated portion of the filter is stable in time; the portion that had not been irradiated during deposition showed a marked shift in optical performance.

The effect of ion bombardment on both ZrO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$ filters is an increase in the absorption of the filters. This is due to the preferential removal of oxygen in the films as they are being deposited, and a subsequent decrease in the oxidation of the film material. The result is an increase in absorption. These results have been for argon ion bombardment. In an attempt to improve the oxidation of the films, oxygen ions were used. The results, however, still show that there is more absorption for the ion bombarded regions than for the regions not bombarded with oxygen ions.
Figure 5-12. Spectrophotometer trace, baked sample.

Upper curve, the reference curve, represents 100% transmittance. The four lower curves are measurements on the sample.
Optical Analysis of Single-Layer Samples

The spectrophotometer traces of single-layer samples of both TiO$_2$ and ZrO$_2$ are in agreement with the results previously discussed. However, to this point no information concerning indices of refraction has been discussed. Additional information on single-layer films is available from the optical monitor traces that had been made during the deposition of the single layers. As discussed in Chapter 4, if no absorption is present in a thin film, then the index of refraction of a film/substrate assembly can be determined if the index of the film and the index of the substrate are known. The reflection from the assembly and hence the transmission can then be calculated.

It is also possible to use this procedure in reverse order. That is, if there is no absorption, then the reflection from the film surface can be determined by subtracting the transmission from unity, taking into account the reflection from the back surface of the substrate. Knowing the reflection enables one to calculate the effective index of the assembly, and if the index of the substrate is known, then the index of the film can be calculated.

If absorption is present in the films, the calculations become more complex. Although attempts have been made to calculate optical constants using computer routines, they have not been useful for analyzing the data obtained from spectrophotometer traces of the single-layer samples made for this research. The largest problem is that the reflectivity from both the front and rear surfaces as well as transmission through the sample must be known for a given wavelength.
Because of the construction of the Cary spectrophotometer, it is difficult to obtain these data for the same spot on the film. After transmission values are recorded, the sample must be removed from a holder and placed in a separate holder for reflection measurements. In addition, the balance of the system must be adjusted, and it is difficult to achieve a 100% line for reflection.

An approximation method has been used to obtain optical constants (Manifacier, Gasiot, and Fillard, 1976). Figure 5-13 shows a typical transmission spectrum for a single thin film. It can be seen that there are two transmission limits that enclose the peaks. Although this curve is a plot of transmission versus wavelength, it could also be a plot of transmission versus wavelength divided by thickness of the film. Using the values of $T_{\text{max}}$ and $T_{\text{min}}$ for a given thickness, $t$, the absorption coefficient can be calculated using the equation

$$\alpha = \frac{C_1[1 - (T_{\text{max}}/T_{\text{min}})^{1/2}] - C_2[1 + (T_{\text{max}}/T_{\text{min}})^{1/2}]}{C_2[1 + (T_{\text{max}}/T_{\text{min}})^{1/2}] - C_2[1 - (T_{\text{max}}/T_{\text{min}})^{1/2}]}$$

where

$$C_1 = (n + n_0)(n_1 + n)$$
$$C_2 = (n - n_0)(n_1 - n)$$

where $n$ is the index of the film, $n_0$ is the index of the incident medium, and $n_1$ is the index of the substrate. The absorption coefficient, $\alpha$, is related to the imaginary part of the index of refraction, $k$, by the equation
Figure 5-13. Transmission spectrum of single layer film.
\[ \alpha = \exp \left( -\frac{4\pi k t}{\lambda} \right). \]

The real part of the index of refraction is given by

\[ n = \sqrt{N + (N^2 - n_0^2 n_1^2)^{1/2}} \]

where

\[ N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \left( \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}} \right). \]

Using these equations, optical constants were calculated for the single-layer samples. The results are shown in Table 5-1. Two samples were prepared with neither UV irradiation nor ion bombardment. The index of refraction for ZrO\(_2\) was found to be 1.905; a table of materials lists the index as 2.05. For TiO\(_2\) the calculation yields 2.193; the table gives 2.2. The effect of UV irradiation is to increase the index of refraction of the ZrO\(_2\) to 1.955. The TiO\(_2\) sample showed a slightly lower index but had much lower absorption. For films that have high absorption, a broadening effect often causes the index to increase, and this is the case for the TiO\(_2\) sample that had not been UV irradiated or ion bombarded.

The effect of ion bombardment was always to increase the index of refraction. For ZrO\(_2\), taking into account the effect of absorption, the index increased with increasing ion powers; the highest index was 2.068. Martin et al. (1983) measured an index of 2.07 with relatively the same amount of absorption. For TiO\(_2\), the highest index was 2.35, but for this sample the absorption was rather high owing to argon ion bombardment. For oxygen ion bombardment, the absorption was improved by about an order of magnitude and the index was 2.22.
Table 5-1. Calculated Optical Constants for Single-Layer Samples

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Note: Each index given is mean index for entire film up to specified thickness.
Optical Birefringence

Early narrowband filters made for this research showed a double peak (Figure 5-14) rather than the single peak transmission line expected for the filter. Through the use of a matched pair of polarizers that could be placed in the Cary spectrophotometer and rotated, it was determined that the filters display birefringence. That is, there are two indices of refraction depending on whether the transverse-electric (TE) or transverse-magnetic (TM) field is analyzed. The amount of birefringence can be determined by measuring the maximum shift in peak wavelength while rotating a polarizer.

The origin of the birefringence is due to the columnar nature of the deposited films, and the principal axes of the dielectric tensor are along the columnar direction \( n_3 \) and normal to the columns both in the plane of incidence of the vapor \( n_1 \) and normal to this plane \( n_2 \). For films deposited normal to the substrate, the birefringence should be uniaxial with an optical axis normal to the substrate surface. It is therefore difficult to detect this birefringence by the use of normal incidence measurements. For films deposited at an oblique angle of incidence, the birefringence should be biaxial with the optic axes in the plane of incidence of the vapor during the film growth.

Several measurements were made to determine the amount of birefringence. The only measurements made while the films were still under vacuum were done by removing the monitoring filter from the optical monitoring system of the Balzers 760 and inserting a mirror.
Figure 5-14. Double peak in narrowband filter.
The light from the optical source that travels through the completed narrowband filter within the vacuum chamber and onto this mirror was then put through a small monochromator. By rotating a polarizer in the output of the monochromator and watching with the unaided eye, the extremums of peak wavelength were recorded. Because of the rough method with which this was done, a number of measurements were made by two observers, and the results averaged. No statistical analysis was made on these observations. Two narrowband filters made of TiO$_2$ and SiO$_2$ were analyzed in this way. Before air was admitted to the vacuum chamber, the separation of the transmission peaks was 45 Å. After air was admitted to the chamber, the separation was 25 Å. This measurement is in agreement with the theory of columnar growth discussed thus far. That is, the voids are originally empty and the index of refraction of the material/void combination is a maximum. When moisture penetrates into these voids, the effective index is reduced.

Another means of measuring the amount of birefringence is with the modified FECO apparatus discussed in the previous chapter. Using this method, the separation of peak wavelengths for TE and TM modes was also found to be 22%. In fact, even this reduction is consistent with the model since moisture has had a chance to further penetrate the sample. Additional measurements made with the FECO have shown that there is greater birefringence in the irradiated than in the nonirradiated regions of the filter. If a narrowband filter is heated in an oven at 125°C for more than 48 hours, the initial
birefringence of the irradiated region is 35 Å versus 20 Å for the nonirradiated regions. For samples that had been ion bombarded, the results were a bit ambiguous. The penetration of moisture with time changes the amount of birefringence with time. Also, the peak wavelength of a filter in a bombarded region is different from the peak wavelength in regions that had been only mildly bombarded. It is not clear if a smaller separation of peak wavelengths for TE and TM modes in a bombarded region can be compared with a slightly larger separation of peak wavelengths in a nonbombarded region that has a higher peak transmission wavelength. Measurements must be taken in vacuum to interpret these results.

Transmission Electron Microscope

A limited number of samples were examined using the carbon replication procedure discussed in Chapter 4. The purpose of using the transmission electron microscope (TEM) is to see if either UV irradiation or ion bombardment changes the columnar structure of films. For a deposition angle of 27.1°, the tangent law predicts that the angle measured between the substrate and the columns of a film should be 14.4°, as illustrated in Figure 5-15. Although several of the TEM photographs clearly show the multilayers of a thin film assembly, it is difficult to see the exact columnar shape. In Figure 5-16, two separate magnifications show a ZrO2/SiO2 narrowband filter that has been neither irradiated with UV nor bombarded with ions. The broad plateaus seen in the photographs are the amorphous SiO2 layers,
Figure 5-15. Thin film growth simulation for deposition angle of 27.1°.
Figure 5-16. TEM photographs of ZrO$_2$/SiO$_2$ narrowband filter.

(a) Microscope magnification factor $15 \times 10^3$
(b) Microscope magnification factor $48 \times 10^3$
which often break in this characteristic pattern. Figure 5-17 shows a ZrO$_2$/SiO$_2$ narrowband filter that has been ion bombarded. Figure 5-18 shows a ZrO$_2$/SiO$_2$ narrowband filter that has been irradiated with UV. Note that in this case the entire cross section of the filter can be seen without the presence of plateaus.

Adhesion, Hardness, and Durability

One purpose of this research was to investigate not only improvements of the optical characteristics of thin films, but their physical characteristics as well. On the macroscopic level, these physical characteristics are adhesion, hardness, and durability. To look for improvement in adhesion, the "Scotch tape test" was used. However, all films showed good adhesion based upon this test. To look for improvements in hardness, the "eraser test" was used. Again, all film samples showed resistance to abrasion based upon this test. Finally, in the area of durability, a number of samples were subjected to high humidities for a period exceeding 72 hours. In addition, a number of samples were heated in an oven for 72 hours. In both cases, no degradation of samples was observed. Although these tests were unable to show any improvement in macroscopic physical characteristics due to either UV irradiation or ion bombardment, they do point out one reason for the popularity of the refractory oxide materials used for this research: They adhere well to the substrate and to each other.
Figure 5-17. TEM photographs of ZrO₂/SiO₂ narrowband filter, ion bombarded.

(a) Microscope magnification factor $18 \times 10^3$
(b) Microscope magnification factor $70 \times 10^3$
Figure 5-18. TEM photograph of ZrO$_2$/SiO$_2$ narrowband filter, UV irradiated.

Microscope magnification factor $18 \times 10^3$
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Many parameters affect the vapor deposition of thin films. The most important of these are substrate temperature, gas pressure, and the geometry of the substrate in relation to the source materials. Thin film growth models have demonstrated that these parameters can be described in terms of the limited mobility of the condensing vapor material and a shadowing effect due to the molecules already deposited. As a result, thin films grow in columns, with voids between the columns. Atmospheric moisture readily penetrates these voids and changes both the physical and optical properties of the films. Any attempt to improve the performance of the films must be based upon either changing the mobility of the condensing atoms or modifying the self-shadowing. Two possible methods of increasing mobility are UV irradiation and ion bombardment during the film growth.

The impact of UV irradiation is small; however, several effects have been noted. X-ray diffraction analysis indicates that UV irradiation has little effect on ZrO₂, but it causes TiO₂ films to become more amorphous. Spectrophotometer results indicate that UV irradiation reduces the amount of absorption in ZrO₂ films and slightly increases their index of refraction. For TiO₂ films, there is little reduction in absorption, but they do show a greater stability in time.
The impact of ion bombardment on ZrO₂ films is to increase the crystalline order, as evidenced by an increase in the tetragonal (111) peak. However, TiO₂ films quickly become amorphous with even slight ion bombardment. Optical measurements indicate that ion bombardment increases the absorption in both ZrO₂ and TiO₂ films. This is due to the removal of oxygen from the growing films. The use of oxygen ions in place of argon ions decreases this effect. Ion bombardment does increase the index of refraction of both ZrO₂ and TiO₂, indicating an increase in the packing density of these films.

A number of recommendations can be made to follow up on this research:

(1) Because of the rapidity with which moisture begins to be adsorbed within a film after it is removed from the vacuum chamber, only optical measurements made while the thin film is still under vacuum will be reliable in determining film structure. It had been anticipated that a scanning monochromator would be constructed for use during this research, but the device was not completed. When it has been integrated into the Balzers BAK 760 vacuum plant, both quartz crystal information and optical transmittances at multiple wavelengths will be available as the thin films grow. This information will aid in determining the impact of both UV irradiation and ion bombardment during film growth.

(2) The present UV irradiation system should be improved by focusing a more intense spot upon the substrate. Although techniques of measurement upon a small spot are more difficult, experience with ion bombarded samples indicates the problem is not insurmountable.
(3) The use of a small UV laser should be considered as an alternative to the mercury-xenon lamp in order to increase the UV irradiation on the substrates. Since ion bombardment increases the crystalline structure of ZrO₂, this material should be examined carefully under conditions of increased UV irradiation.

(4) Attempts should be made to improve the oxidation during deposition of TiO₂ when ion bombardment is used. This could be accomplished by increasing the background oxygen pressure, although this will cause added wear on the electron beam gun filaments. Higher oxygen pressures within the ion gun itself should be attempted, while at the same time the extraction voltage should be reduced to minimize etching of the growing films.

(5) An ion source should be obtained that provides a more uniform ion flux over the area monitored with the scanning monochromator. This will eliminate the averaging that occurs when only a small region is modified by ion bombardment.

(6) Additional materials should be examined. These should include metals as well as dielectric materials.

(7) Since this research has confirmed that even small perturbations of the deposition conditions can modify growing films, other techniques should be attempted. For example, other researchers have suggested using a piezoelectric crystal to "vibrate" the substrate during deposition. Small movements may be able to disrupt columnar growth and improve the packing density.
APPENDIX A

OPERATIONS CHECKLIST FOR BALZERS BAK 760
AND RELATED EQUIPMENT

Prior to operation, accomplish the following:

(a) Clean interior of vacuum chamber with vacuum cleaner and replace foil on walls if necessary.
(b) Replace/replenish source materials.
(c) Load substrate(s).
(d) Change quartz crystal if necessary. (Quartz crystal should be replaced when reading on digital control is 150000 or higher.)
(e) Change optical monitor plate(s). If it is anticipated that several monitor plates will be needed, ensure that there are a sufficient number loaded into the monitor plate changer assembly.
(f) Close door of vacuum chamber and hold in place using two handles.

A. INITIAL PUMPDOWN

1. Obtain 160-liter tank of liquid nitrogen from cryogenics lab; attach liquid nitrogen line to tank. Open valve 3/4 of a turn (this is to prevent wasting the liquid nitrogen by splashing in the cryo-pump).

2. Push PUMP button on pumping station control system (PC 101).
The roughing pump will first pump down the cryo-pump until set point A is reached, as indicated by an illuminated indicator on TPG 070. When this is reached, the roughing pump will begin pumping down the vacuum chamber and liquid nitrogen will fill into the cryo-pump.

Set point B determines when a sufficient vacuum has been reached for the cryo-pump to take over for the roughing pump. Set point C determines when the roughing pump has reached a sufficient vacuum for any valve to open. The pressures for the set points are determined by the odd-numbered knob settings; the actual set points are determined by the small set screws in conjunction with the even-numbered knob settings.

3. Open hot water output line; open hot water supply line; push PUMP/HEAT on pumping control system. Hot water will circulate through coils on vacuum chamber and promote outgassing of contaminants.

4. When cryo-pump is cooled to 16 K, as indicated on gauge above cryo-pump, the valve between the cryo-pump and the vacuum chamber will open. The best procedure is to let pumping continue overnight; when the plant was commissioned, the minimum pressures reached were $1 \times 10^{-7}$ mbar on the pump gauge and $5.5 \times 10^{-6}$ mbar on the chamber ionization gauge (IMG 060B). (The ionization gauge can be set to read either linearly or logarithmically; LOG(BLUE) is normally selected. For more accurate
readings, set the switch to LIN(BLUE) and select the proper range on the LIN. RANGE switch.)

B. PRIOR TO COATING RUN

1. Push PUMP button on pumping station control.

This turns off the hot water to the vacuum chamber. Turn off hot water inlet valve; turn off hot water outlet valve.

2. Turn on chilled water supply.

Turn on chilled water outlet valve; turn on chilled water inlet valve; push PUMP/COOL button on pumping station control; turn on outlet valve to ion gun (if installed); turn on inlet valve to ion gun; check that chilled water pressure gauge in chase (marked A) reads 90 to 95 psi. (If it does not, open bypass valve marked B until it does.)

CAUTION: Pressure should not exceed 100 psi.

3. Turn on cold water supply.

Turn on cold water outlet valve; turn on cold water inlet valve.

4. Turn MAIN SWITCH on first rack to ON (1). (This supplies power to the substrate heaters and to the electron guns.)

5. Push HEATER MAINS button on second rack. Select substrate heater temperature by means of thumb switches to left of button.
Temperature is indicated on digital display (ETD 101) in rack 1. This promotes any remaining outgassing of contaminants.

CAUTION: Ensure that substrate holder is rotating in order to protect it from warping.

6. When ionization gauge shows desired pressure, coating run can begin.

C. COATING OPERATION

1. Accomplish glow discharge in chamber.

This should be done immediately prior to beginning coating run. It is easiest to accomplish this procedure automatically, as follows:

a. Program L1/T1 to 600 (seconds) on KB 101. All control entries are made by selecting one of the four blue buttons (L1, L2, L3, L4) and one of the yellow buttons. (See p. 5 of Balzers manual BG 800 089 BE for a description of each.) Numbers are entered in keypad and displayed on bottom digital display; when the correct value has been entered, push ENT button to enter into memory. Any mistakes can be erased by pushing CLR button.

b. Program L1/T2 to 999999. (This is treated as infinity by the electronics.)

c. Program L1/N to 100000. (This tells the computer that parameters for source 1 (i.e., L1) are to be used first.)
d. Set to automatic operation by turning lower toggle switch on BL 101 to up and triggering upper toggle switch once. CONT light should illuminate.

e. Push RUN button. (Valve will open, allowing air to enter vacuum chamber until a pressure of about $4 \times 10^{-2}$ mbar is reached. Throttling control under IBM Personal Computer should be on, with switch set to AUT.)

2. Allow chamber to return to proper vacuum upon completion of glow discharge. Push RUN button to stop execution of program; substrate rotation will continue.

While chamber is returning to vacuum, warm up optical monitor source, UV source, etc. Optical monitor lamp is turned on by first depressing POWER switch, then depressing LAMP ON switch. Program desired values into digital controller if using automatic operation. Typical values for SiO₂, ZrO₂, and TiO₂ are given in Appendix B.

3. After proper vacuum pressure is reached, bleed in oxygen to desired pressure.

Turn on oxygen bottle valve and regulator. Turn on valve control unit RVG 040. Turn SET POINT to desired value; valve will open when valve voltage reading is 8. Adjust pressure to desired value by turning SET POINT and watching chamber pressure on ionization gauge.
4. If the IBM Personal Computer is to be used for either quartz crystal or optical monitor information, turn it on. Turn on the toggle switches for the quartz crystal and the optical monitor, located below the IBM unit.

5. Begin coating using either automatic or manual operation.

D. AUTOMATIC OPERATION

NOTE: For automatic operation, toggle switch on both electron gun controls must be set to CONST. RATE.

NOTE: Electron guns will not operate if the six lights at the top of rack 1 are not illuminated. TUBE WATER light out indicates cold water is not on. DOOR light out indicates back door of rack 1 is open. KEY LOCK light out indicates back door is not properly latched. In addition, GUN WATER light on each electron gun control must be illuminated; if they are not on, either the chilled water is turned off or it is not turned to a high enough pressure.

1. If using large crucibles, push ROTATION button on both crucible controls (ETS 110).

2. If using the four-pocket crucibles, rotate proper source material into position by pushing SOURCE 1 (or 2, 3, or 4 as appropriate).

3. If using the crescent-shaped portion of the oscillating crucible, depress OSCILLATE button and select proper speed of oscillation.

4. Reprogram L1/T1 to 0 and L1/T2 to 0. This will prevent glow discharge from starting.
5. Set reflectance reading on optical monitor to 92% (if using glass substrate) using FINE ADJUST.

6. Begin program operation by pushing RUN button.

7. Monitor program execution.

CAUTION: Look at source through front sight windows to ensure that electron beam is striking source material. To reposition beam, use BEAM POS. knob on remote controller. The top gun control is for source 1 and the bottom control is for source 2. The spread of the beam can be controlled by AMPL. LONG. and AMPL. LAT. knobs on electron gun control unit; the frequency of the sweep is controlled using FREQ. LONG. knob.

NOTE: The amount of time elapsed or remaining is indicated on the top digital display of rack 2 by depressing the green T button. Prior to a shutter opening, the time display indicates the amount of time remaining for T1+T2+T3+T4. After the shutter opens, the time display indicates how long the shutter has been open. Time is in seconds.

NOTE: Quartz crystal information is displayed on the top digital display by depressing one of the remaining green buttons. XT gives the difference between 5 MHz and the actual quartz frequency. R gives the deposition rate in angstroms per second. TH gives the thickness in angstroms. The left-hand digit is the source being used.

NOTE: If the layer thickness is incorrect as indicated on the optical monitor, the value can be reentered during program operation. Be sure to select the proper blue layer button along with the yellow button marked TH. Values are entered using the procedure described in step C1a.

8. Upon completion of automatic operation, rotate substrate holder stops. To prevent warping the substrate holder, return toggle switch to manual position and trigger toggle 1 on OU 101 control to rotate substrate holder.
E. MANUAL OPERATION

NOTE: Quartz crystal information is not available during manual operation.

CAUTION: If it becomes necessary to quickly stop the evaporation because of a lack of material, etc., the EMISSION OFF button on the remote control serves as an emergency off switch.

1. Turn bottom toggle switch on digital controller to down. MAN light should illuminate.

2. Turn on substrate rotation using toggle switch 0.

3. Toggle switches 0 thru 11 on OU101 are used as follows:
   
   0 Rotation of substrate holder
   1 Glow discharge
   2 Source 3 (left-hand thermal source)
   3 Source 4 (right-hand thermal source)
   4 Shutter 1 (left, rear)
   5 Shutter 2 (right, rear)
   6 Rotation of crucible for source 1
   7 Rotation of crucible for source 2
   8 Shutter 3 (left, front)
   9 Shutter 4 (right, front)
   10 Source 1 (left-hand electron gun source)
   11 Source 2 (right-hand electron gun source)

   An illuminated light indicates that shutter is open or power is on.

4. Thermal sources are operated by toggling switch 2 or 3, as appropriate, to turn power on, then toggling either CHANNEL 3 (for left-hand thermal source) or CHANNEL 4 (for right-hand thermal source) to select proper power level. Toggling the switch up increases the power by about 1%; toggling it down decreases power by about 1%. The small LEDs indicate the amount of power
selected. They go up in steps of about 10%; i.e., if the third LED from the bottom is illuminated, the power is about 30% of maximum value. The appropriate shutter is opened when the source material has melted into the tungsten coil.

5. Electron gun sources are best controlled manually by selecting CONST. EMIS. position of toggle switch on electron gun control. Top electron gun control panel is for left-hand electron gun; bottom electron gun control panel is for right-hand electron gun. Electron gun sources are used as follows:

a. Depress green ON button on top drawer of rack 1 to turn off high voltage.

b. Depress green ON button of electron gun control to turn on filament.

c. Use EMISSION knob on hand-held remote control to turn up power for selected source; monitor condition of beam and source by watching through sight ports.

d. To melt a particular area of source material, stop rotation by depressing ROTATION button on crucible control. The two buttons at the top of the remote control rotate the crucible either clockwise or counterclockwise.

NOTE: If a particular source of the four-pocket crucible has been selected, the crucible control unit may rotate the crucible automatically to try to position the correct source back into position. To override this, depress the ROTATION button twice, then use the remote control unit as needed.

e. Open the appropriate shutter (toggle switch 4 or 5).
f. Monitor the deposition using the optical monitor and noting quarter-wave points.

6. Upon completion of coating, rotate emission controls on both remote units fully counterclockwise. This will prevent accidentally turning on power to the electron guns when starting a new coating.

7. Turn off power to filaments by depressing OFF button on each gun control unit. Turn off high voltage by depressing OFF button on top panel.

F. AFTER COATING RUN

CAUTION: Chilled water should remain on until chamber has cooled.

1. Turn off substrate heaters by depressing HEATER MAINS button; light will go out.

2. Ensure that substrate holder continues to rotate until chamber has cooled.

3. Turn off oxygen bleed valve by turning SET POINT to 0. Do not turn off toggle switch until valve voltage has reached zero.

4. Turn off regulator and main valve on oxygen bottle.

5. Turn off optical monitor by depressing LAMP OFF and POWER buttons.
6. Turn off rotation or oscillation of crucibles.

7. Turn MAIN SWITCH on rack 1 to off (0).

8. Turn off cold water supply line; turn off cold water output line.

9. When the vacuum chamber has cooled to at least 70°C, shut down the chilled water supply as follows:
   a. Turn off inlet valve to ion gun.
   b. Turn off outlet valve to ion gun.
   c. Depress PUMP switch on pumping station control.
   d. Turn off chilled water inlet valve.
   e. Turn off chilled water outlet valve.
   f. Reduce chilled water system pressure to about 80 psi by turning bypass valve B counterclockwise; monitor using gauge A.

10. To remove samples from chamber, depress VENT button on pumping station control. If chamber will be open for awhile, circulate hot water through chamber walls by opening hot water inlet valve and hot water outlet valve, and depressing VENT/HEAT (white) button.

11. After vacuum chamber has reached atmospheric pressure, depress either STBY button or STBY/HEAT (green) button. This will close the inlet valve to the chamber but keep the cryo-pump operating properly.
12. After removing samples, push PUMP button to pump down system.

13. If more than 18 hours will elapse before the next coating run, shut down the system by pressing OFF after the vacuum chamber has reached a pressure of at least $5 \times 10^{-2}$ mbar. (The 18 hours represents a tradeoff between the amount of liquid nitrogen it takes to initially cool down the cryo-pump and the amount of liquid nitrogen it takes to keep the cryo-pump cooled down.)

NOTE: After the system has been shut down, depress the REG button to regenerate the cryo-pump. The ballast valve on the roughing pump should be engaged during regeneration, which should last several hours. When regeneration is complete, again depress the REG button.

G. KRATOS UV POWER SUPPLY

CAUTION: To protect from a build-up of ozone, turn on the fan under the vent hood.

1. Set current adjust to position M. Ensure that the proper patch plug (white for mercury-xenon lamp) is installed on the back of the power supply.

2. Turn power on.

3. Ignite lamp by depressing LAMP START button; do not hold down for more than 2 seconds.

4. After lamp comes on, adjust current to 27 A.

5. After voltage reaches 36 V, turn on cooling fan.
H. ION GUN

1. Connect proper gas supply to inlet valve; open main valve and regulator valve on bottle.

2. Supply gas to ion gun by opening valve under the vacuum chamber. If the vacuum plant has reached a sufficient vacuum and air is not being bled into the chamber, the ionization gauge can be used to estimate the ion gun gas pressure.

3. Turn on both power switches on power supply unit.

4. Turn up discharge voltage until current registers; turn voltage knob until desired current is reached.

5. Turn up beam voltage to desired value.
APPENDIX B

TYPICAL AUTOMATIC DEPOSITION PARAMETERS

Three dielectric materials were used for this research. The input values for the digital controller for automatic deposition are as follows:

<table>
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<tr>
<th>Input</th>
<th>Units</th>
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<th>TiO$_2$</th>
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<td>P4</td>
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</table>

NOTES: Layer thickness depends on substrate temperature and is calibrated by using optical monitor to watch for turning points.

Depending on which material is deposited first, the value for T1 for that material is set to 600 and the value for T2 is set to 999999. After glow discharge is complete, these values are reset to 0 so the glow discharge will not be repeated.
APPENDIX C

THE INVERTED MAGNETRON ION SOURCE

The ion source used in this research is a cold-cathode, magnetically enhanced discharge source, in which ions are extracted through an aperture in the cathode wall. After extraction, the ion beam is collimated and focused by a system of electrodes. Although only argon and oxygen were used for this research, the source is capable of producing a beam of ions of a variety of materials that are in a gaseous form at room temperature.

The ion gun, designed by B. Singh and D. Boyarsky of Denton Vacuum, Inc., is referred to as an inverted magnetron ion source because of the geometry of the discharge. A description of the construction of the ion gun is aided by a view of the disassembled device and the cross-sectional view shown in Figure C-1. The device consists of a cylindrical stainless steel cathode (A), 25 mm in diameter and 30 mm long, in which a coaxial stainless steel anode (B) of 3-mm diameter is mounted. The anode is insulated from the cathode with ceramic insulating bushings (C). These bushings fit into apertures in the cathode end plates (D). Also mounted onto the bushings are two ring magnets (E). These magnets are made of cobalt-samarium and have pole-face magnetic field strengths of about 2 kG; one pole face is in contact with the end plates (D) of the cathode. The magnetic field produced inside the cathode is coaxial with the ion source and has a
Figure C-1. Inverted magnetron ion source.

A Stainless steel cathode  
B Stainless steel anode  
C Insulating bushing  
D End plate  
E Ring magnet  
F Ceramic spacer  
G Block  
H Gas pipe  
I Extraction electrode
value of about 300 G in the center. Two ceramic spacers (F) used in conjunction with two threaded stainless steel blocks (G) serve to clamp the whole assembly together and make it gas-tight. The gas to be ionized is introduced into the cathode through a stainless steel pipe (H) of inner diameter 2 mm and outer diameter 4 mm, which is soldered into the cathode wall. Although the ion gun can be used in the "self-extraction" mode, a more intense and focused ion beam is obtained by the aid of an additional extraction electrode (I).

The cross-sectional view of the ion gun, Figure C-1, also shows the electrical connections and target location. Also shown in the figure is the magnetic field, which is perpendicular to the plane of the paper. This field is co-axial with the ion source and is perpendicular to the applied radial electric field. A stabilized DC power supply of 0 to 5 kV and 0 to 100 mA is connected between the cathode and anode. A second stabilized DC power supply is used to extract the ion beam, and does so by means of a bias on the first extraction electrode, which is negative with respect to the cathode. The cathode, second extraction electrode, and target are all grounded.

Gas is introduced into the cathode, and owing to thermal ionization both electrons and ions are present. The positive ions are accelerated across the discharge gap and strike the cathode surface with enough energy to liberate electrons by means of secondary electron emission. These emitted electrons accelerate toward the anode and ionize more neutral gas atoms enroute, thus creating more electron-ion pairs that are accelerated in the discharge volume.
An ionization avalanche takes place, and subsequently a steady electric discharge is established between the electrodes. This discharge is characterized by three distinct regions. At the electrodes, charged particle concentration regions called "sheaths" are formed, and quasi-neutral plasma fills the main inter-electrode volume. In this plasma region the electron and ion densities are equal, and the variation of the electric field is quite small. Almost all of the applied voltage falls across the cathode, or Langmuir sheath, which is usually a few millimeters wide, and conditions of this sheath are very critical for discharge stability. The third region is the anode sheath, and it also determines the stability of the discharge; however, it is not well understood and continues to be examined (Singh, 1978).

The discharge of this ion source is very efficient, as it produces a stable ion beam at relatively low chamber pressures. This is best explained by considering the motion of the electrons in the discharge. Once liberated from the cathode surface, the electrons are accelerated across the cathode sheath and enter the plasma with virtually the same energy. The electron motion is divided into essentially four components:

1. Helical Motion Along B Field Lines. Here, the emitted electrons are tied to magnetic field lines and gyrate around them. Since they also travel along these lines, the resultant path is helical.

2. Reflection from Cathode End Plates. Because of the negative potential of the cathode and the gradient in the magnetic field, the electrons are reflected back and forth between points where the lines enter the cathode surface.
3. E and B Drift. Throughout the discharge volume, both the electric and magnetic fields are mutually perpendicular. Thus a Lorentz force is exerted on the electrons, causing them to move in an azimuthal direction.

4. Anode Drift. Here the electrons "jump" from one magnetic field line to the next in the direction of the anode. Since they collide with neutral gas molecules and are affected by the electric field, the electrons eventually reach the anode.

Essentially, the electrons are trapped in the discharge volume, oscillating back and forth along field lines, traveling in azimuthal paths, thus greatly increasing their path length and lifetime in the system. In an efficient electron trap, the electrons that reach the anode are incapable of further ionizing; that is, their energies are degraded by successive collisions to below the ionization threshold energy of the neutral gas.

The positive ions also experience the same forces, but owing to their much greater mass and slower speeds their motion is quite different than that just described. Essentially the ions accelerate to the cathode in paths that are only slightly curved. Some of the ions that are incident on the cathode surface are extracted through a small aperture drilled into the cathode wall. The negatively biased electrode serves to accelerate and focus the ions. Because the extraction voltage and ion beam current are independently variable, the ion source is extremely versatile.

To obtain values of ion current at the substrate for various values of ion beam current and extraction voltage, a stainless steel target was positioned in front of the ion gun at about the same distance as the bombarded substrates. By means of two pins of an
electrical feedthrough, one lead of an ammeter was attached to the target and the remaining lead attached to the grounded substrate holder assembly. The currents measured for both argon ions and oxygen ions are included in Table 3-1.
### APPENDIX D

**SAMPLES AND DEPOSITION CONDITIONS**

<table>
<thead>
<tr>
<th>Run</th>
<th>Source</th>
<th>Treatment</th>
<th>Substrate temp, °C</th>
<th>Oxygen pressure, torr x 10^-4</th>
<th>Ion gun settings, kV/mA</th>
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<td>Discharge   Beam</td>
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*Spacer only

**Interior
APPENDIX E

TURNING POINT DATA FOR SINGLE MATERIAL COATINGS

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<th>Matl, treatment</th>
<th>Percent reflectance at given wavelength*</th>
<th>λ/4</th>
<th>λ/2</th>
<th>3λ/4</th>
<th>λ</th>
<th>5λ/4</th>
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*Where two values are given, second value is thickness of coating, in Å. All runs made starting at a reflectance of 92%. 

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Messier, R. (1982), Private communication, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.


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