

THIN-FILM OPTICAL COATINGS

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1. INTRODUCTION

Vacuum deposition processes are those most commonly used for the construction of optical coatings. Although the films that are produced are solid, there are many significant differences between them and bulk materials and especially in the microstructure of the films. Thermal evaporation, the most widely used process, produces an intensely columnar microstructure that includes a large proportion of pore-shaped voids that have far reaching effects on the properties of the films, optical, thermal, mechanical and chemical. The energetic processes that involve an element of ion bombardment during film growth have been shown to produce a much more compact microstructure, eliminating many of the problems associated with the columnar structure. However, the microstructure still differs in important respects from that of similar bulk material and still exerts an influence on thin film properties

2. COLUMNAR MICROSTRUCTURE

The columnar microstructure of optical coatings is a consequence of the relatively low substrate temperature during deposition, which limits the mobility of the material condensing into the thin film. The film then grows as an array of columns because migration of the condensant into the shadows of the columns is suppressed. Figure 1 shows a typical columnar microstructure. Such a microstructure has a profound effect on the optical properties of the film¹. An isolated column of dielectric material of refractive index rather higher than its

surroundings, which is placed in an electric field, becomes polarized. The charge sheets that form on the outer surface tend to reduce the field within the material and force it into the surroundings. A film made up of isolated columns with low refractive index material surrounding them, exhibits this effect in all columns so that the net refractive index of the composite film is reduced. An expression for the refractive index of an array of separated cylindrical columns is due to Bragg and Pippard² and can be written:

$$n_f^2 = \frac{(1-p)n_v^4 + (1+p)n_v^2 n_s^2}{(1+p)n_v^2 + (1-p)n_s^2} \quad (1)$$

where we use p for the packing density, n_s for the index of the solid part of the film and n_v for the index of the void material surrounding the solid columns. It is also possible to visualize a microstructure where the effect of the surface charge sheets is completely suppressed such as will an intimate mixture of two materials, or simply a columnar structure with very high packing density. In such cases an expression for refractive index of the composite film is:

$$n_f^2 = pn_s^2 + (1-p)n_v^2 \quad (2)$$

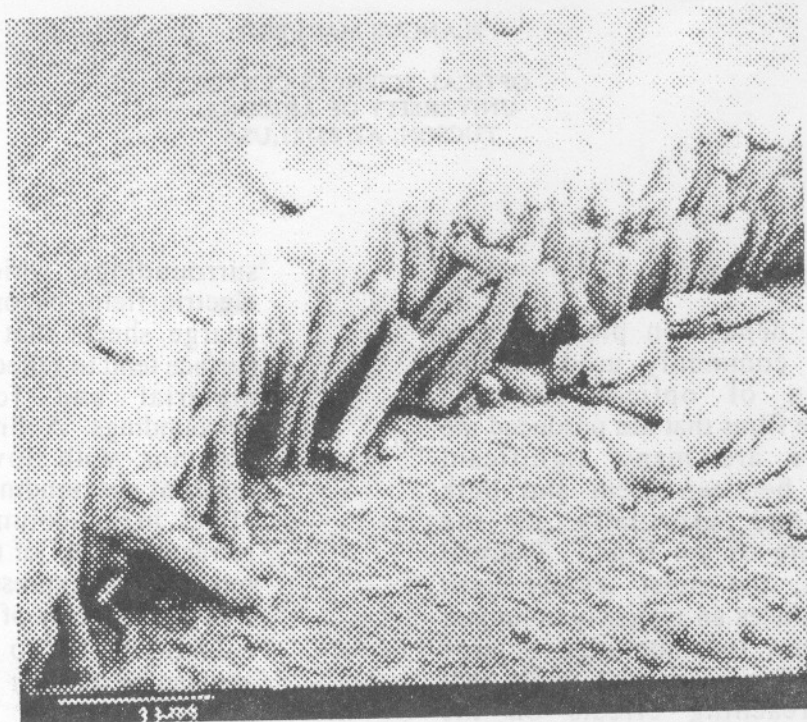


Figure 1. A zinc sulfide film showing strong columnar structure³.

Curves are shown in figure 2 along with some measured results for zirconia^{4, 5}. The results for one series of measurements show a shift from the mixture law at high packing density to the Bragg and Pippard at low packing density, indicating a pronounced columnar structure. The other series shows a typical mixture result down to quite low packing densities. Here the columnar form is not so pronounced. This illustrates the sensitivity of film optical constants to their microstructure and to their deposition conditions.

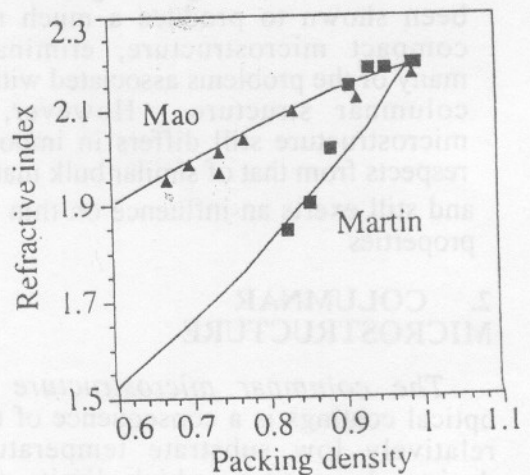


Figure 2. Measured zirconia refractive index as a function of packing density. Mao⁵ results measured in air and compared with the refractive index of a mixture of solid and water-filled voids. Martin⁴ results measured in vacuo and compared with the Bragg and Pippard model with vacuum or air-filled voids

The columnar structure is clearly anisotropic, and this leads to anisotropy in film properties that are influenced by the microstructure. The most important of these for optical coatings are the optical properties themselves and strong form birefringence can, and often does, occur in optical films⁶. This form birefringence is most often uniaxial with optic axis parallel to the columnar axes, normal to the film surface. However, deposition conditions can be arranged so as to tilt the columnar direction with respect to the film surfaces. Then the columns tend to depart from their symmetrical shape and the form birefringence becomes biaxial and can be very pronounced, much greater than intrinsic crystalline birefringence. It is possible that devices could be developed to make use of this effect.

The columnar structure, with its voids in between the columns, adsorbs atmospheric moisture⁷, first by surface adsorption of a tightly bound, essentially monomolecular, layer of moisture and then at higher relative humidities by capillary condensation. This leads to shifts in the optical characteristics towards longer wavelengths that depend on relative humidity. The moisture rarely penetrates evenly into multilayers but forms a scattered set of expanding circular patches of optically altered wet material.

Material that is of low packing density, in which the material is arranged in arrays of columns cannot be as rugged as corresponding solid material and poor abrasion resistance, poor adhesion and high internal strain energy tends to result.

3. ION ASSISTED DEPOSITION

The defects of conventionally-deposited films have led to the introduction of energetic processes for the deposition of optical coatings. These include sputtering, ion plating and ion-assisted deposition, and their major characteristic is that additional energy is given to the condensing film in the form of bombardment by energetic ions and, sometimes, increased kinetic energy of

the condensing molecules⁸. Ion-assisted deposition is the simplest of these processes and consists simply of thermal evaporation with bombardment of the growing film by ions, with energies usually around several hundred electron volts. The bombardment, and, where appropriate, the additional evaporant energy, induces movement of the film material so that the voids are squeezed out and the film is rendered much more solid. It has been theoretically demonstrated by advanced computer modelling^{9, 10} that the major effects are due to the additional momentum of the molecules, either supplied by collisions with the incoming energetic ions, or derived from the additional kinetic energy of the evaporant. Experimental evidence exists¹¹ that shows correlation of the effects with momentum rather than energy of the bombarding ions. Major benefits of these processes are the increased packing density of the films, making them more bulk-like and hence increasing their ruggedness, the improved adhesion resulting from a mixing of materials at the interfaces between layers, and a reduction of the sometimes quite high tensile stress in the layers. The increase in packing density reduces also the moisture sensitivity and can actually eliminate it altogether¹². The increased packing density also improves the stability of the films in other ways. Magnesium fluoride films resist high temperature oxidation better, for example¹³. The hardness and corrosion resistance of metal films, especially with dielectric overcoats¹⁴, is improved by ion-assisted deposition but the optical properties tend to be adversely affected, possibly by the implantation of a small fraction of the bombarding ions¹⁵. The increased reactivity of the bombarding ions permits the deposition of compounds, such as nitrides¹⁶, that are difficult or impossible by normal vacuum evaporation.

4. OTHER ASPECTS OF MICROSTRUCTURE

A second level of microstructure in optical thin films is their crystalline state. This is less well understood than the columnar microstructure but considerable progress has been made. Optical thin films are deposited from vapor that has been derived from sources at comparatively very high temperature. The substrates on which the films grow, are at relatively very low temperature. There is therefore a great lack of equilibrium between growing film and arriving vapor. The film material is rapidly cooled or quenched, and this not only influences the formation of the columnar microstructure but it also affects the crystalline order. The material that is condensing will attempt to reach the equilibrium form appropriate to the temperature of the substrate, but the correct rearrangement of the molecules will take a certain time, and the film will tend to pass through the higher temperature forms during this rearrangement. If the rate of cooling is greater than the rate of crystallization, then a higher temperature form will be frozen into the layer. The very rapid cooling rate normally existing in thin films implies the presence of quite high temperature forms and there are often mixtures of phases. This explains an, at first sight, curious behavior of thin films. Frequently there is an inversion in the crystalline structure in that at low substrate temperatures a predominance of high-temperature crystalline forms are found, whereas at high substrate temperatures, more low temperature material appears to form. The low substrate temperature leads to a higher quench rate and the rest follows. Amorphous forms, corresponding to a quite high temperature, can often be frozen by very rapid cooling, and are enhanced by a higher temperature of the arriving species. For example sputtering, where additional kinetic energy is possessed by the arriving molecules, often gives amorphous films. The new low voltage ion-plating technique¹⁷, again

with high incident energy, appears virtually invariably to give amorphous films. The high temperature forms are often only metastable and may change their structure at quite low temperatures leading to problems of various kinds. Some films deposited in amorphous form by sputtering may sometimes be induced to recrystallize, in a manner described as explosive, by a slight mechanical disturbance, such as a scratch, or by laser irradiation¹⁸.

Samarium fluoride has two principal crystalline forms, a hexagonal high-temperature form and an orthorhombic low temperature form. The table shows the results of thermal evaporation and ion-assisted deposition which both lead to this apparently inverted structure¹⁹. Zirconia has three principal structures, monoclinic, tetragonal and cubic in ascending temperature. Klinger and Carniglia²⁰ found that very thin zirconia shows a cubic structure, but becomes monoclinic when thicker than a quarterwave at 600nm. This behavior can be explained by a lower rate of quenching when the film is thicker and less thermally conducting. Alumina, normally amorphous in thin film form, can recrystallize in the electron microscope when subjected to the electron bombardment necessary for viewing²¹. Zirconia has been shown to exhibit similar behavior²².

Samarium Fluoride (SmF₃)¹⁹

Normal high temperature form	Hexagonal
Normal low temperature form	Orthorhombic
Thermal evaporation Substrate temperature 100°C	Hexagonal (111)
Thermal evaporation Substrate temperature ≥200°C	Orthorhombic (111) with some hexagonal
Ion assisted deposition Substrate temperature 100°C	Hexagonal (110) with some (111)
Ion assisted deposition Higher bombardment at substrate temperature 100°C	Hexagonal (110) with appearance of new peak SmF ₂ (111)?

Thin films, therefore, are complicated mixtures of different crystalline phases, some being high-temperature metastable states. Such behavior is clearly very material and process dependent and each specific system requires individual study. What is a good structure for one application may not be so for another. The low scattering of the amorphous phases may make them attractive for certain applications but their high-temperature or high-flux behavior may not be as satisfactory.

5. MECHANICAL PROPERTIES

As we move towards the mechanical properties of thin film, our knowledge and understanding lessen. We tend to talk in the thin-film field as though stress were an attribute of a particular film, some materials being compressive and some tensile, for example. The stress in the film is a complicated function of the various phases and the way in which they are packed together, different

crystallites with perhaps different stress, in turn dependent on deposition conditions, and on the surrounding material that, for equilibrium, must support the total stress. We pay a great deal of attention to the reaction forces at the substrate, which tend to distort it, and will often look for material combinations and deposition conditions for multilayer coatings that will combine to minimize the substrate forces. The low shear loading across the substrate-multilayer interface does imply that adhesion failures there are less likely. However, a net low stress in a multilayer does not necessarily mean low shear stress at all interfaces, nor low tensile or compressive stress in all layers. A set of parallel springs can be in equilibrium and yet the individual springs can be alternately in significant tension and compression. A film system can similarly exhibit dangerously high stress at certain interfaces even though the total stress is low. It is not always at the substrate that adhesion failures occur.

In mechanical engineering, there is good understanding of materials and their behavior, of fracture, of deformation and of ways to ensure the continued integrity of a system. A simple stress versus strain curve for a material together with indications of its variation with temperature are indispensable prerequisites for the successful use of an engineering material in a structure that is to be subjected to mechanical, and possibly thermal, loading. Even something as simple as a stress versus strain curve does not exist for thin-film materials. Yet, in use, they are subjected to comparatively enormous loads, sometimes originating externally, but frequently having their origin in internal strain energy. Ruggedness of thin-film systems must remain, therefore, a completely empirical matter, unless the basic design data necessary for a detailed quantitative engineering approach can be generated. Part of the problem is the difficulty of deriving a stress versus strain curve for a thin film material. Most attempts that have been made, vary the temperature so that differential contraction or expansion of film and

substrate generates the necessary loading. This creates, usually, more problems that it solves.

Figure 3 shows the behavior of a simple aluminum film subjected to a cycle of temperature from room temperature to 275°C and back²³. Stress is measured interferometrically by the deflection of the thin silica substrate and here is in units of fringes. During heating the film becomes compressively loaded to the extent that it deforms plastically but at the elevated temperatures, diffusion may also be a factor in a rearrangement of the material, either in the form of grain growth or protrusions on the surface. The curve is similar to results obtained by Townsend and Vander Plas on aluminum with small copper additions²⁴.

The situation with dielectric materials can be still more difficult. Thermal stress cycles, in vacuo, of zirconia deposited under identical conditions on silicon substrates, except that in one case an assisting beam of argon ions bombarded the film, are shown in figure 4⁵. The first puzzle is why the stress should be tensile when ion-assisted deposition usually moves film stress towards compressive. Here the tensile stress in the ion bombarded film is actually greater than the corresponding unbombarded film. Furthermore, if the assumption is made that the change in stress is entirely attributable to the expansion coefficient of zirconia, then estimates of the expansion coefficient can be made. Results for the two films are shown in figure 4⁵ and clearly this is not a convincing explanation. It is more likely that phase changes are being induced in the films both by changing temperature and by bombardment. Clearly much more needs to be done to understand the effects, not only in zirconia, but in all the materials that are used in thin film systems.

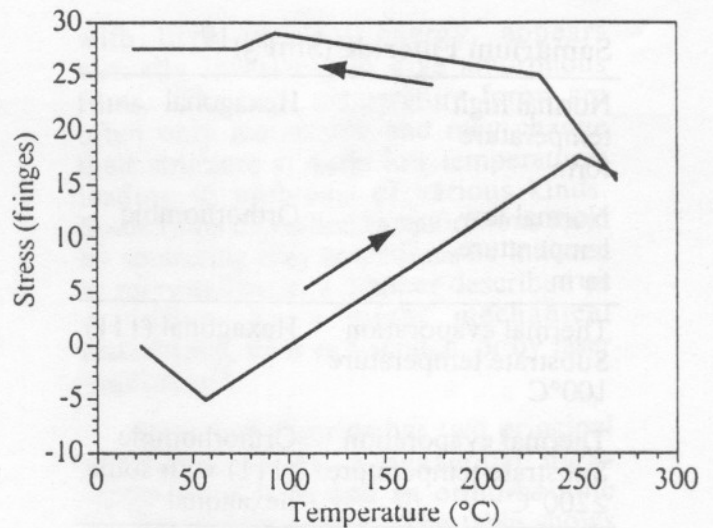


Figure 3. The stress behavior of an aluminum film under temperature cycling²³.

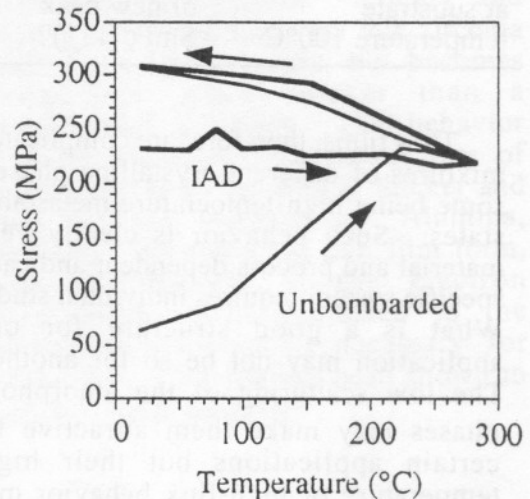


Figure 4. Thermal stress of zirconia films⁵. Both films were deposited at a substrate temperature of 150°C and rate of 0.4nm/s. The upper film was bombarded additionally with 1000eV oxygen ions at 200 μ A/cm². The stress in both cases is tensile.

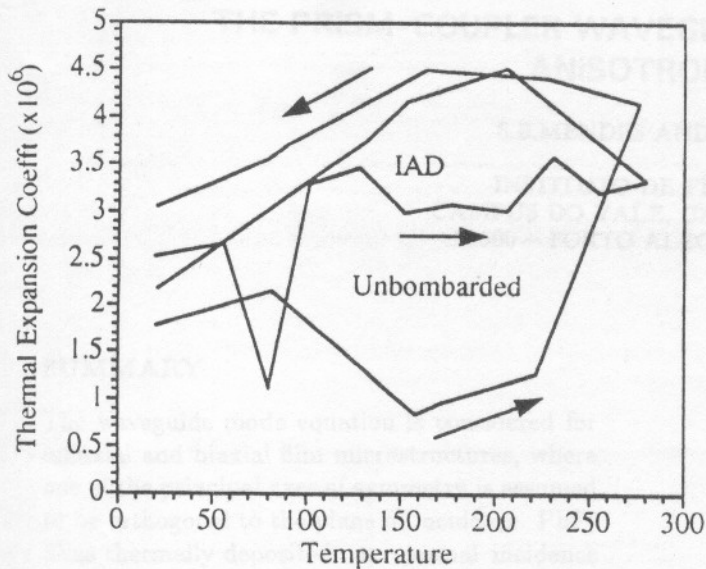


Figure 5. The expansion coefficient of the zirconia films derived from the measurements in figure 4⁵.

6. CONCLUSION

The conclusion that we can draw from all this, is that there is still much that we do not understand about optical coatings, and that there is still much to be done. The elimination of the worst features of the columnar structure by the introduction of the energetic processes such as ion assisted deposition has been a considerable step forwards, but it has not solved all the problems.

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7. REFERENCES

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