

## Introduction

*Two different applications and procedures for coatings and materials are discussed in this issue. Demands placed on the coating industry for optical and mechanical (wear-resistant) and also coatings for the semi-conductor industry sometimes require performance that cannot be satisfied by existing coating materials. In this case, coatings must be engineered from known or common materials. Solid materials grown in thin film form fall into two general classifications, depending on application: passive as for the majority of optical and mechanical coatings, and active, as for electro-optical applications. The latter include transparent conductive coatings and photo-active coatings. The brief discussions presented here will introduce the reader to these alternate thin film technologies.*

## Structured Coatings and Nano-Engineered Materials

For those special cases where a material or a deposition process does not produce all the required properties, materials and their structures can be manufactured to satisfy the need. The concept and practice of tailoring the structure of a thin film to modify its properties is not new. Chemical etching or ion exchange at the surface of glass is a well known technique for obtaining a refractive index low enough to provide some degree of surface reflection reduction. Perfect AR of glass of index 1.52 requires a coating of index 1.23, lower than any solid thin film material. However, chemical etching to introduce a surface layer on glass that is permeated with microscopic air-filled cavities can approach this effective low index. Similarly, leaching heavy ions from the upper surface layer of soda lime glass can also reduce the effective index. While these surface-modification techniques are simpler and less expensive methods for anti-reflecting glass than vacuum deposition, the resultant surfaces have low mechanical and cleaning durability.

Most fluoride compounds and oxide compounds, when grown under conditions of low adatom energy and thus low surface mobility, form a columnar microstructure. Under typical deposition conditions, the substrate is rotated in a two-axis

planetary motion to average the variety of vapor-stream incidence angles, thus causing the columns to grow perpendicular to the substrate. Another older concept recently re-introduced for controlling the structure of thin solid films is that of altering the deposition (incidence) angle during film growth, whereby the columns grow at an oblique angle to the substrate and the microstructure of the film layer grows to be inhomogeneous and anisotropic. Shadowing among the growing columns produces an open, porous structure that is generally undesirable because of its low cohesive strength and tendency to adsorb water and other vapors on the column walls, leading to instability of optical properties. The growth conditions that favor a columnar microstructure can be exploited to create "sculptured" films for special purposes. For example, with slow rotation about specific rotation axes, helical structures can result. Without rotation, a tilted linear structure of isolated columns results. Dichroism is observed in oriented anisotropic optical films to make polarizers. Some applications of these anisotropic structures are as film-type two-dimensional polarizers or retarders, surfaces for orienting liquid crystal materials, as chemical agent detectors, micro-channel biosensors, pressure transducers, microelectronic devices. [1, 2] Ori-

ented anisotropic magnetic and piezoelectric films can also be produced.

The ‘microstructure’ of a deposited thin solid film is characterized by its orientation and crystal phase. Columnar layers are composed of micro-crystals predominately randomly assembled and stacked in a vertical column whose width generally tapers from wide at the substrate to narrow at the top due to shadowing by neighbor columns. The micro-structure can be either growth or nucleation controlled, and influenced by substrate temperature and roughness, and adatom energy. In nucleation-controlled growth selection, the micro-structure of the grown layer is determined by that condensing micro-structure that possesses the highest nucleation rate. This rate is influenced by substrate surface state and energy. Specifically, surface contamination can increase the energy barrier to nucleation; surface defect density is directly related to nucleation site density; and surface mobility is related to arrival energy. In growth-controlled microstructure selection, all thermodynamically possible crystalline states have equal nucleation probability, but those that have a higher growth rate will propagate and predominate in spite of a mixed initial

interlayer of competing phases. This type of microstructure often exhibits inhomogeneity in its optical properties ( $n$  &  $k$ ) with thickness. Other undesirable features of crystalline micro-structure films is their higher stress and lower packing density and high internal surface (grain boundary) area leading to environmental and mechanical instability.

Some oxide compounds are known to exhibit inhomogeneous optical properties because of the particular micro-structural growth selection as described above. Notable among these are  $ZrO_2$ ,  $TiO_2$ , ITO,  $CeO_2$ , and other refractory oxides. One method of reducing or eliminating the problem is to introduce ‘impurities’ that serve to destroy single or large-size crystal growth and thus produce a structure with no long-range order. Such a structure is essentially amorphous, and exhibits a more compact, dense micro-structure. Often glass-forming materials such as silica, MgO or yttria are added. Past issues of CMN have described such mixed or composite materials, which are available either as solid solution preparations or produced by co-evaporation / co-sputtering.

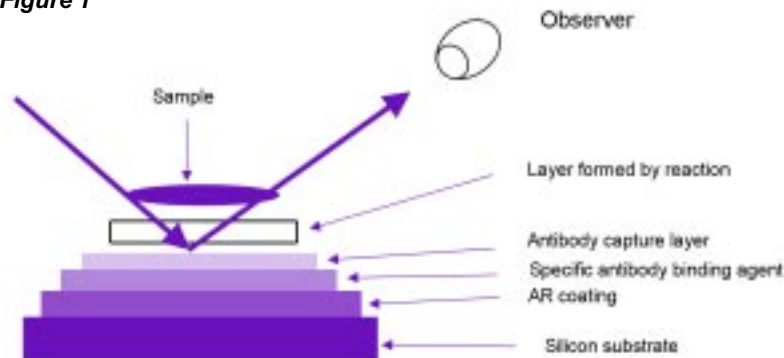
A different technique for producing

growth-controlled micro-structures is the process of depositing nanolaminates. In such a structure, many alternating nanometer-thickness layers of two materials are deposited under conditions that control the growth nature of each layer. Individual layer thicknesses range from  $\sim 2$  nm to  $\sim 20$  nm. This engineered thin film structure is useful for creating nucleation, transition, or buffer layers between materials of otherwise incompatible chemical, physical or mechanical properties (TCE, or lattice mismatch being two examples). Nanolaminate architectures composed of rf-excited reactive sputter-deposited  $TiO_2$  and  $ZrO_2$  layers were investigated in recent research [3]. The thermodynamic evolution of  $ZrO_2$  polymorphs crystallizing from a melt follows the trend: cubic ( $2360^\circ - 2680^\circ$  C) to tetragonal ( $\sim 1075^\circ - 2360^\circ$  C) to monoclinic ( $\leq 1075^\circ$  C). The question explored was how the microstructure of  $ZrO_2$  evolves as a function of the relative  $ZrO_2 / TiO_2$  layer thicknesses and the total number of layers. When the thicknesses were  $\leq 4$ nm / 1.5 nm respectively, no crystal order was present for a bilayer count up to 68. Only with  $ZrO_2$  thickness increased to  $\sim 11$  nm and 25 bilayers was cubic  $ZrO_2$  detected. The single c- $ZrO_2$  crystallite spanned several bilayers. Increasing the  $TiO_2$  layer thickness causes other crystal morphologies to be suppressed. Thus, it is possible to engineer and control the properties of the nanolaminate.

Thin film biosensors are used for the rapid immunoassay detection of infectious diseases and viruses in the physician’s office or hospital. The principle of operation is the appearance of a color change when a specific biologic agent is present. The detector is

*continued on page 3*

**Figure 1**



## TiO<sub>2</sub> as a Reactive Coating

While the majority of thin film coatings are used as passive elements, some coating materials generate specific responses or initiate reactions when excited by external stimuli. Titanium dioxide, a material that CMN has discussed frequently for optical applications, falls into the category of reactive coatings. Another example is vanadium oxide, whose reflectance changes with temperature. The wide band gap and the variety of possible crystal phases of TiO<sub>2</sub> are properties responsible for its useful reactivities, among which are: photocatalysis, hydrophobicity, and organic decomposition (anti-bacterial and engine oil) ability. These properties make titania films also useful for applications such as window self-cleaning and defogging. Incident light of energy greater than the ~3 eV band edge of titania generates holes and electrons. These carriers produce the oxidation and reduction reactions on the surface of titania layers responsible for photocatalytic activity.

Films for photocatalytic applications have been commonly produced by CVD (sol-gel deposition), but anti-fog films for automotive rear-view mirrors are now being deposited by rf magnetron sputtering on unheated substrates [5]. It has been found that the titania anatase structure provides greater photocatalytic activity than the rutile phase, therefore deposition parameters are adjusted to predominately favor the anatase structure. Crystalline phase formation and order are dependent on the total pressure during sputtering; higher pressure forces the anatase phase over the rutile phase. The ratio of O<sub>2</sub> to total pressure has a smaller influence on phase, but does affect morphology, an important factor in the reactivity of the coating. Higher relative O<sub>2</sub> pressures create rougher films of lower packing density and therefore higher surface area. One indication of photocatalytic activity is the reduction in contact angle between the TiO<sub>2</sub> surface and water as measured in the dark after UV irradiation. For example, for rutile, the contact angle after irradiation is 42°; that for porous anatase films is as low as 10° three hrs after irradiation. The minimum film thickness for effective activity is ~200 nm [6]. The films exhibit an increase in contact angle with time in the dark, but the anatase films showed a lower rate of increase. The decomposition efficiency of the anatase phase is also greater than the rutile phase as indicated by the increase in transmission of a methylene blue coating or rapid decomposition of an oil film on the titania surface. Conversion of the films to the rutile phase the photocatalytic activity decreases substantially.

### Structured Coatings...from page 2

a substrate coated with an interference layer that reflects a particular color that then shifts when an antigen is reacted with a specific enzyme. The reaction causes the precipitation of a layer whose optical thickness optically interferes with the thin film coating to cause the color shift. Figure 1 shows a simplified diagram illustrating the composition of a thin-film bioassay sensor [4]. The silicon substrate is coated with an anti-reflecting layer of silicon nitride or Diamond Like Carbon (DLC) tuned in combination with

the biological attachment polymer and antibody capture layers to anti-reflect a portion of the visible spectrum. As the sample and reagent react, an optically transparent layer is formed that causes selective reflection of a color indicative of the thickness and thus the concentration of the biological agent. DLC is useful because of its efficient biological capture ability. Other metals and their oxides are used as required for different target assays. The detection limits of optical biosensors range from ng/ml to pg/ml.

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