

In this quarter's CMN, we discuss the deposition of all-important Silicon dioxide films, including the never-ending quest to control mechanical stress in thin films, and the creation of colored reflection films for decorative functions.

Silicon Dioxide Films

Silicon Dioxide, SiO₂, is the common low-index layer material in oxide-based optical coatings for the spectral range ~250 nm to ~2500 nm. It is paired with high- and mid-index layers such as TiO₂, Ta₂O₅, Nb₂O₅, HfO₂, ZrO₂, Al₂O₃, and others. Maximization of the High-to-Low index ratio in a multi-layer design results in a smaller layer count, broader spectral response, and generally greater design flexibility. SiO₂ can be deposited by E-beam from a solid disk or granules of fused silica. The surfaces of these source materials are melted by the sweeping E-beam, and evaporation proceeds to grow oxidized film layers without the need for additional oxygen. Because melting occurs to a shallow depth, local hole drilling occurs with consequential narrowing of the vapor beam distribution. Continuous motion of the solid disk source or a controlled sweep pattern is required to maintain a broad evaporation source throughout the deposition. Silicon dioxide films can also be grown by reactively evaporating

silicon monoxide from a resistance-heated (R. H.) or E-beam-heated source from which the vapor is created by sublimation. An oxygen background pressure high in the 10 e-05 Torr range is required to produce oxidized films. This reactive method has been shown to produce films with lower absorption and better vapor stream distribution than is produced by evaporation from fused silica source materials. Depositing SiO₂ by R.H. from a SiO baffle box provides a consistent vapor stream because there is no surface to erode as there is when using E-beam evaporation. Ion assisted (IAD) or plasma-ion assisted (PIAD) processes are added to E-beam or R. H. evaporation to promote oxidation and increase packing density. Dense silicon dioxide films are also reactively sputter-deposited from a silicon target and oxygen-rich plasma. CERAC Technical Data Sheets provide guidance in evaporation parameters [1]. A general guideline for materials deposition appears in the Photonics Handbook [2].

Favorable attributes of SiO₂ films are: they provide the lowest index oxide film layers, they are easy to evaporate or sputter, and exhibit high laser damage threshold and good environmental stability. As is true of nearly all oxide compound film layers, SiO₂ exhibits compressive intrinsic stress. As a result, oxide pairs accumulate a dominant compressive strain. We have discussed in previous CMN issues the effects of stress on mechanical strength, cohesion, adhesion, and environmental stability, and presented methods to reduce film stress. The stabilities of the mechanical and optical properties of film layers especially need to be considered when coatings are subjected to high laser energy fluences. For example, film defects such as micro-cracks are defect sites that can initiate damage under high-energy laser exposure. We refer readers to previous CMN articles that discussed the relationship between nano-structure and the origin and characteristics of intrinsic film stress. Single materials prop-

erties and the advantages of mixtures of oxide compounds and mixtures of fluoride compounds are frequently discussed in CMN. Unfortunately, any additive to silicon dioxide will result in increasing its film index, however, the advantage to be gained is reduced intrinsic stress. Small percentages of aluminum oxide have been co-sputtered or co-evaporated with silicon dioxide to reduce stress.

Processes involving high energy deposition techniques such as IAD, PIAD, or sputtering that produce high packing densities also increase compressive stress. Therefore in practice, a balance must be established between the film stress local (inter-layer) environment and factors such as external environmental stability and laser damage threshold. Several phenomena influence film stress, primary among them are: deposition process (and parameters), the nature of and progression of growth nano-structure, and post-deposition thermal and moisture exposure. An ideal microstructure would be amorphous, defect-free, dense, and possess neutral intrinsic stress. Such a film layer grown on a substrate whose physical properties are decoupled from the film (an impossible scenario, to be sure) would be immune to thermal and humidity changes and to laser-induced damage threshold.

A recently published study, "The evolution of stress in evaporated silicon dioxide thin films"[3], helps us understand the parameters that influence the nature and magnitude of film stress. The stress in a growing SiO₂ film was monitored in the coating chamber during deposition, evaporation paused, slow venting, and atmospheric exposure. Thickness, rate, pressure, and temperature were dependent variables plotted vs. film thickness up to 350 nm. As is true for many oxide compounds, SiO₂ film grows with compressive stress. We summarize the changes reported in compressive stress resulting from varying

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Which Process Deposited Coatings with Lower Stress: Evaporation or Sputtering?

If you thought you would find the answer here, sorry to disappoint you. If you thought you would find the answer in the voluminous technical literature that covers this subject, sorry again! The growth process is as important, if not more so, than the deposition technique. Ideal film morphology can only proceed under conditions of thermodynamic equilibrium, and such conditions do not occur in real-life depositions. Influences such as substrate and film defects, impurities introduced in the condensing material or by the deposition atmosphere (composition and density), and the kinetic energy of the arriving species and ionic or reactive component cause film growth morphology to deviate from the ideal. The structure-zone model (SZM) describes film growth as a function of energy and surface temperature as related to melting temperature [4]. Surface tempera-

ture influences mobility, and defects initiate nucleation sites. When a film covers the surface, diffusion processes on the surface and between microcrystalline grains influence growth morphology.

Most of the studies of stress in thin films have been done using pure metal depositions because of their simplicity in comparison to the growth of compounds. A current review of growth models has been published by R. Koch [5]. To summarize, the major difference between the two deposition techniques that determines morphology and consequently stress is the addition of kinetic energy, described as 'atomic preening', in the sputtering process. When conditions support low mobility for example at low substrate temperatures or with material incompatibilities that form a high density of defects, compressive stress is produced. When high mobility exists, the defect density can reduce by diffusion and migration, and reduce the magnitude of compressive stress. The energy imparted to the growing film is affected by amount of scatter determined by the sputtering pressure. At high pressures, kinetic energy is lost among the high density of gas molecules, thus creating fewer defects and resulting in lower compressive stress. The arriving adatoms are said to be 'thermalized' and

have energies approaching that from evaporation. Stress level can therefore be adjusted, or moderated, between levels of tensile and compressive by controlling sputter pressure.

Models and mechanisms that explain stress generation in evaporated films are more complex than those for sputtering. Similar mobility and pressure effects apply, but the adatom energies are smaller, and are perhaps a fraction of an eV compared to 2-10 eV for plasma sputtering. Grain boundary or column formation and coalescence give rise to tensile stress. Other defect features and the incorporation of gases and water vapor also contribute to result in tensile stress dominating over compressive. Diffusion along grain boundaries and relaxation of internal forces tend to reduce the tensile component, however. The addition of energy by IAD or PIAD to the thermal energy of evaporation produces high packing density, and increases tensile stress. It appears that a lot more investigative work is necessary to help us understand process-related stress, especially for evaporated thin films.

These studies and the generation of growth models are useful in aiding our understanding and visualization of the origins of stress in thin films. They direct attention to the deposition driving parameters that drive stress production.

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the deposition parameters. The nominal parameters were P: 7.5 e-5 Torr (0.01 Pa), 200°C, 0.5 nm/s. Variations in parameter values showed interesting trends. For all variations, stress became increasingly compressive as thickness increased from 0 to ~50 nm, then reversed to become less compressive. Nearly neutral stress was produced for the higher pressure of 2.2 e-04 Torr at 200°C, and 0.5 nm/s rate, but became as large as -400 MPa for 1/10 that pressure. At lower pressures, larger final compressive values resulted for thickness >~100 nm. Cooling also increased compressive stress. Upon exposure to atmospheric pressure and humidity, the stress in SiO₂ films continued to decrease (becoming less compressive) and reached a steady value ~80 MPa after 8 hr exposure. The evolution of stress upon exposure to air is a complex process, apparently following two stages [3]. Initially water and air molecules permeate the pores of the film and increase compressive stress. When the pores are saturated, reactions between SiO₂ and H₂O relax the compressive component and the resultant film stress is reduced. This model is not inconsistent with our suggestion that additives ("dopants") and mixtures of materials promote dense layer growth by reducing the internal nano-structure energy that otherwise would produce columnar structures with large void volume. (Refer to past discussions of oxide compound mixtures and fluoride compound additive compositions). Materials engineering with additives promotes dense amorphous and environmentally stable film growth and avoids the stress level expected for crystalline nano-structure. As a technique to counter the normally high stress resulting from high-energy deposition processes such as IAD and PIAD, this approach deserves further study. The respective roles of the deposition technique and the micro-structure in creating film stress is a continuing topic of study among thin film researchers.

Colored Decorative Coatings

There are many applications for bright coatings that reflect a colored tint. All-dielectric multi-layer reflectors can be made that are based on quarter-wave reflecting stacks of alternating high-and low-index layers. Such reflection filters require many layers and good thickness control. To obtain saturated reflection, the transmitted energy needs to be discarded, typically by absorption. Reflection filters based on the use of semi-reflecting / semi-transmitting metals are used as decorative coatings, and can be applied to transparent or opaque substrates. These coatings are often deposited on metal substrates, and onto molded plastic parts made for cars and household appliances. The production of selectively colored reflectors using thin metal films is not a new idea; many papers and patents have been published since about 1948 [6]. The basic idea is to use a semi-transparent metal sandwiched in a reflection cavity built of dielectric layers that are tuned to reflect a narrow band of wavelengths and give the desired hue. To produce the desired color contrast, out-of-band wavelengths are absorbed in the multiple transmission and reflection passes between the semi-transparent layer and the bottom reflecting metal layer. By adjusting the optical thickness of the dielectric layers and the phase change introduced by the metal layers, the reflected hue and its bandwidth (purity) can be changed. By adjusting the thickness of the semi-transparent metal layer(s), the saturation of the color and its brightness can be controlled. The bottom layer in the stack is an opaque reflection metal, usually aluminum.

Figure 1 illustrates the simplest configuration. Figure 2 shows the reflectance curves and visual colors for reflector designs that simulate the color of gold, and bright purple and green reflected colors. Varying the dielectric layer materials from silicon dioxide to titanium dioxide and their relative thicknesses changes the color that is reflected. The semi-transparent metal used is chromium in thickness 3 to 6 nm, but similar metals having the appropriate extinction coefficient values can be substituted. Alternative metals are rhodium and nickel.

Figure 1. Generic colored reflector design. Chromium is often used for the semi-transparent metal layer. Opaque aluminum is the bottom layer.

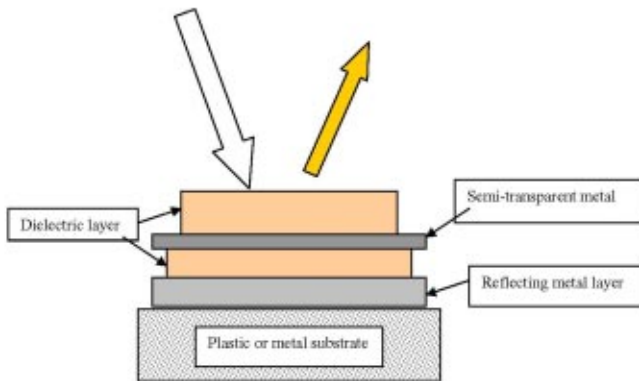
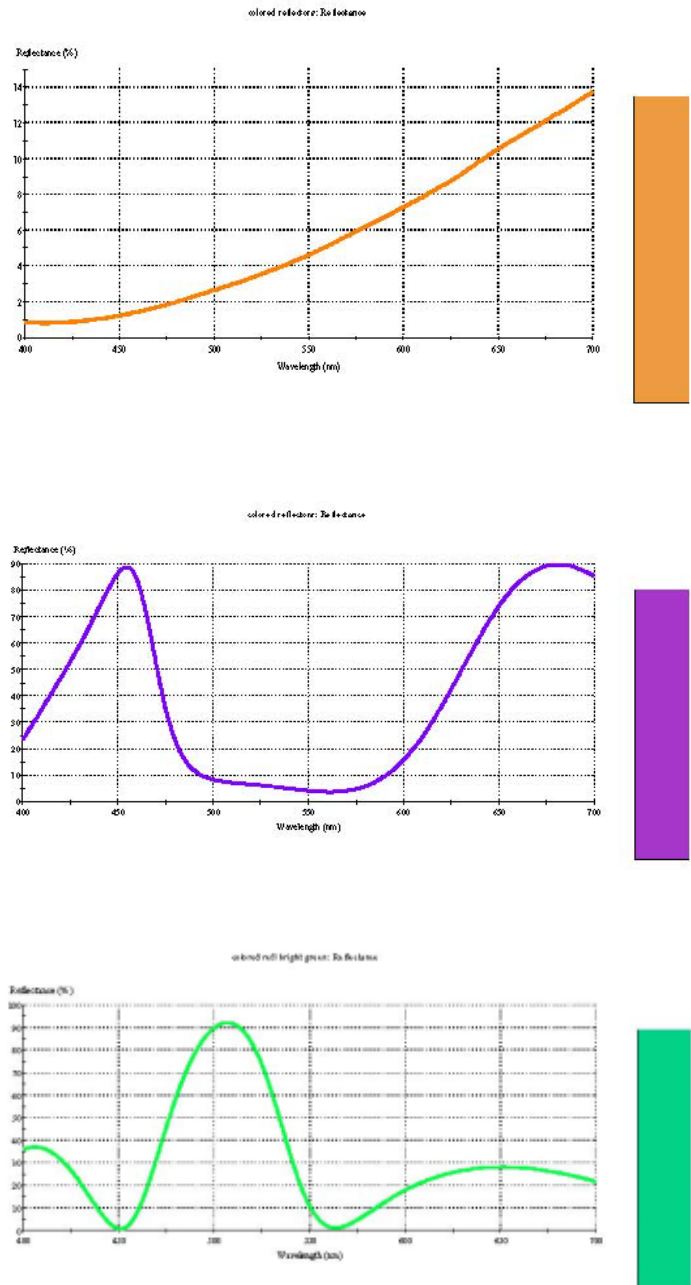


Figure 2. Samples of reflected colors capable of being produced by varying the dielectric and semi-transparent metal layers in the generic design shown in Figure 1.



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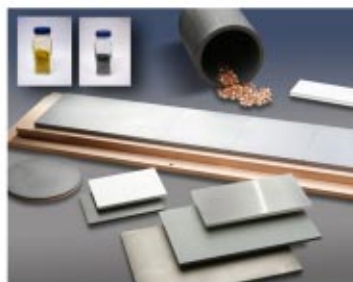
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