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*In the first article of this issue, we address the electrical properties of thin films that find application as resistors, semiconductors, and biosensors. A second topic is the theory of film layer growth, and the parameters involved in producing high quality optical film layers.*

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## High *k* Films

Thin films as applied to electrical device manufacture are not discussed on these pages as often as films intended for optical applications. However, their application and properties are essential for microelectronic circuit gates and devices such as detectors and capacitors. The specific physical properties that "high-*k*" films must possess are high dielectric constant (*k*), high resistivity and low loss tangent ( $\tan \delta$ ). Capacitor insulators, in addition, must possess high breakdown voltage. We have discussed the merits of mixtures of materials to produce optical coating materials with improved properties in previous issues, and we relate the influence on film microstructure below. To summarize, mixtures produce improved stability to environmental attack by their increased packing density and they accomplish this by defeating the tendency to form large-grained crystallites and instead promote dense, amorphous growth with smoother surfaces. For refractory compounds like zirconia and hafnia, the thwarting of crystal growth by adding, for example  $Y_2O_3$ , eliminates temperature-induced crystal phase changes, thus enabling higher temperature operation. Index inhomogeneity is also discouraged. Oxide-compound mixture materials are available as several products made by CERAC and other thin film materials suppliers [1]. Examples of evaporable materials available from CERAC are the refractive index  $n = 2+$  materials: Z-1077 ( $ZrO_2$  and MgO), Z-1092 ( $ZrO_x$  and  $TiO_2$ ), and medium-*n* ( $n \sim 1.65$ ) M-1126 ( $MgO-Al_2O_3-ZrO_2$ ). In addition, CERAC supplies two fluoride-compound low-index mixtures, IRX™ and IRB™. Mixed oxide ceramic sputtering targets are also available.

Mixtures produced by "doping" a host material with small percentages of additives also improve the electrical properties of thin film layers. A study of the electrical prop-

erties of  $TiO_2$  and  $ZrO_2$  as influenced by admixtures of  $Al_2O_3$  and  $SiO_2$  was published [2]. Materials differ in their ability to produce electrically useful films. Compounds that form with high reaction energy are generally stoichiometric in composition. Examples are  $Al_2O_3$ , MgO, and  $SiO_2$ , which possess high dielectric constants. Compounds that form films containing charge defects, however, do not have a balance between their cations and anions; examples with anion vacancies are  $TiO_{2-x}$  and  $ZrO_{2-x}$ . The compounds  $Zn_{1+x}O$  and  $Cr_{2+x}O_3$  have interstitial cations. Non-stoichiometries are created during growth in several ways: by incomplete oxidation, unfavorable temperature, and by the presence of extrinsic impurities (dopants). Films of zirconia and titania with high defect densities are good n-type semiconductors because of the high concentration of free electrons. They find application in gas sensors (oxygen) and catalysis, but possess poor insulating properties i.e., low resistivity. Techniques for controlling the electrical properties of films are being developed for those and other biosensor applications.

To improve on the electrical properties, the researchers [8] sputtered ceramic targets consisting of:  $TiO_2$ -10 vol. %  $Al_2O_3$  and  $ZrO_2$ -10 vol. %  $SiO_2$  to deposit non-stoichiometric films, and compared the properties of the films with stoichiometric films of the pure materials. The results are summarized. For either film composition, substrate temperatures between 200° C and 500° C had no influence on film thickness. However, when RF power was varied from 50 W to 150 W, the pure  $ZrO_2$  grew at a lower rate than either the  $ZrO_2$  mixture or the two compositions of  $TiO_2$ . Structurally, the pure titania films formed the anatase phase with a small amount of rutile phase. The mixture produces an amorphous or a nanocrystalline structure. For the  $ZrO_2$

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films of both compositions, the monoclinic phase was formed. The addition of  $\text{SiO}_2$  to  $\text{ZrO}_2$  enhanced crystallization, while the addition of  $\text{Al}_2\text{O}_3$  to  $\text{TiO}_2$  discouraged crystallization.

The electrical properties of the non-stoichiometric films are apparently more stable against processing parameters such as substrate temperature and post annealing than the pure compounds. Stable dielectric properties and higher resistivities are produced because the incorporated  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions capture oxygen thereby reducing oxygen vacancy and thus carrier concentrations. Another result was noticed: pure  $\text{ZrO}_2$  films fractured after annealing to  $200^\circ\text{C}$ , while the doped films survived to at least  $400^\circ\text{C}$ . The low thermal expansion coefficient of the silica lowered the internal stress of the high TCE of the zirconia. The resistivity of pure titania films increased from  $7 \times 10^6$  to  $3 \times 10^{10} \Omega \text{ cm}$  upon annealing, while for the dielectric-stable mixture the values went from  $2 \times 10^9$  to  $4 \times 10^{12} \Omega \text{ cm}$ . For the zirconia films, resistivity was  $1 \times 10^9 \Omega \text{ cm}$ . For the mixture, resistivity increased from  $8 \times 10^9$  to  $3 \times 10^{12} \Omega \text{ cm}$  upon annealing. Break-down voltages were 4-5 times higher (4-5 MV/cm) for the doped films of both materials than for the pure compositions, independent of annealing. Lower loss tangents were obtained with the mixed compositions while retaining high  $k$  values. For the mixtures,  $k$  was independent of annealing temperature, while it decreased for the pure titania. It is concluded that the electrical properties of thin films can be greatly modified and improved through the use of mixed compounds rather than pure materials.

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## Controlling Deposition and Growth Energetics

We turn our attention now to the deposition of layers that provide specific optical and mechanical properties as solid thin films. Previous CMN issues have discussed the steps in the evaporation / deposition process; here we outline the basic mechanics and energetics involved. In the evaporation process, thermal energy is applied to the solid source material to raise its kinetic energy to the point where the pressure of its vapor exceeds the pressure of the environment ("vacuum" pressure). In sputtering, the kinetic energy of accelerated ions (Ar typically) break atoms or molecules free from the target. The kinetic energy possessed by evaporated species is a few tenths of an eV; that for sputtered species is several eVs. These energies are dissipated at the substrate that is being coated, and participate in the nucleation and growth of the film layer. Substrate heat energy plays a significant role in the energy equation, especially for the case of thermal evaporation.

Depending on the energy available during film growth, very different structures are developed: low-energy processes tend to grow films with a porous microstructure having large polycrystalline structure elements (columns) and weak adhesive and cohesive properties. Films deposited with higher energy, as with sputter deposition, generally possess a denser microstructure with smaller crystalline grains and stronger mechanical binding forces. In current wide-spread practice is the addition of kinetic energy by means of a bombarding beam of highly accelerated heavy Ar ions: the process Ion Assisted Deposition (IAD) is used to enhance the properties of thermally evaporated films. With IAD, energies of hundreds of eV can be added to the growth energies, thus producing packing densities and refractive indices that approach the bulk-like material form. We refer the reader to the Structure-Zone Model presented in CMN V14, Issue 3 (Sept 2004) that illustrates the relationship between energy and film structure.

Other factors enter into the nucleation and growth processes that compete with the rosy picture implied by the simple review just given. The energetic condition of the substrate surface determines both the mechanical and to some degree, the optical properties of the growing microstructure. If the surface on which the film is expected to grow does not present a favorable energy state, nucleation and microstructure will not be optimum. A surface that has a layer of contamination that does not react favorably with the condensing adatoms is an example of a surface that will not promote strong chemical bonding or dense packing. During evacuation and heating, volatiles are released from the coating chamber surfaces and they condense on "clean" substrate surfaces. Atomic cleanliness can be restored by ion scrubbing with an energetic ion source, but ever-present oxygen and water vapor form strong bonds to all reactive surfaces and are difficult to remove. For the case of oxygen-reactive silicate and metallic substrates and metal-oxide condensates, those contaminants participate in and are consumed during condensation and surface reactions. Surface energies need to be higher for bonding to noble metals, fluorides, and sulfide and selenide substrates, however, and often these substrates require the addition of an intermediate "adhesor" layer consisting of a material that has mutual reactivity or of a freshly deposited layer of the substrate material. Examples of useful reactive intermediate layers of thickness  $\sim 100\text{-}200 \text{ \AA}$  are  $\text{CrOx}$ ,  $\text{TiOx}$ ,  $\text{SiOx}$ ,  $\text{Y}_2\text{O}_3$ , etc. Adhesion topics were discussed in an earlier CMN [3].

When the surface energy exceeds a threshold value, adatoms will migrate until they nucleate on favorable active sites. Under ideal conditions, two-dimensional growth covers the surface before vertical growth proceeds. Providing there are no interruptions in the growth dynamics such as temperature, ion energy, atmosphere composition or pressure changes, the film will grow with a homogeneous microstructure. Production of high packing density requires additional energy supplied by concurrent high-energy ion bombardment, as illustrated in the Structure-Zone Model. IAD and sputtering processes are widely used techniques for achieving high packing densities in oxide-compound layers, and small crystallite size with low inherent stress. When all the internal growth-related

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## Film Stress Control

Stress in thin film layers can alter mechanical, optical and electrical properties. Manifestations range from micro-cracking that increases optical scatter and sheet resistance and vulnerability to moisture absorption, to substrate distortion, or to catastrophic lifting from the substrate. The mechanical stress exhibited by thin films is the result of a complex interplay of internal forces that are established during the deposition and growth of the film and external forces that are imposed by the operating environment. A third component can be imposed by differences in thermal expansion coefficient between the film layer and the substrate. The intrinsic stress associated with fluoride films is generally tensile in nature (forces lie in the plane of the substrate and cause contraction to form "dried mud-flat" cracking), while many oxide films exhibit compressive stresses (film expands parallel to the substrate and often buckles). We have some degree of control on the magnitude and sign of the intrinsic stress component, and this control enables us to produce mechanically and optically stable coating/ substrate systems. Deposition conditions provide a tool for engineering stress balance or reduction.

We paraphrase G. N. Strauss [4] in the list of mechanisms responsible for creating and altering intrinsic stresses:

- Formation of lattice defects in the form of volume voids, disorder or defects
- Variation in inter-atomic spacing with regions of differing density
- Changes in film microstructure such as crystal grain sizes, crystal phase transformation
- Incorporation of foreign gas or materials
- Chemical reactions.

Any or all of these mechanisms can evolve during microstructural growth or after deposition. In the growth model summarized above, the initial nucleation stages produce compressive stresses that transition to tensile as the islands of local nucleation coalesce to a continuous layer with grain boundary formation. This scenario proceeds when surface mobility is high. With low mobility, the films tend toward a dominant tensile nature. Bombardment by energetic ions can reduce tensile stress and in some cases change the sign of the force to compressive. Ion energies approaching 100's eV create compressive stress by incorporation into the microstructure and the release of kinetic energy in the film layer. The energy deposited within the layer is a function of the energy of the impinging ions and their flux density. In spite of the complexities involved in the analytic problems of stress analysis, reduction, and compensation, researchers have succeeded in empirically establishing operating parameters for manipulating stresses in single and multi-layer film structures.

A mature technique for reducing intrinsic stress and stabilizing optical films is admixture of a host material with small percentages of a mutually-soluble "dopant", as we described above. The additive discourages large open grain structures, leading to densification and non-crystalline structures as the dopant occupies and completes unsatisfied chemical and mechanical bonds. Dramatic improvements in chemical, mechanical and optical properties have been demonstrated, in addition to the electrical property improvements detailed above for sputtered mixtures. CMN articles discussed two cases where external forces imposed large stresses on thin films: high temperature and

tribological coatings. Solutions were based on two- and three-element mixtures of oxide compounds [5]. Increased laser damage thresholds have also been demonstrated with mixed vs. pure materials [6].

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energy conditions are satisfied and film layers are in the state of their lowest energy, they are also resistant to external stresses. The result is a stable film that exhibits bulk-like optical and mechanical properties: the ideal film.

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