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In this issue, we discuss work reported in papers that deal with topics of high current interest. One is mechanical stresses in coatings induced by two environmental influences. The other topic is Al:doped ZnO, a transparent conducting coating. Efforts are in progress for developing AZO layers with sheet resistance lower than ~100 Ω/sq, and we review one recently published effort toward that goal.

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Environmental Influences on the Mechanical Properties of Oxide Films

A popular topic in these *CERAC Coating Materials News*letters is the durability of thin films. Thin film coatings are applied to the surfaces of optical materials to modify their optical and mechanical properties. Film layers that provide protection and decoration are applied to metal and polymer surfaces. Layers only a few µm thick can modify the mechanical properties to the degree that resistance to scratching and to other forms of abrasive wear has been increased many times over that of the bare substrate.

We have discussed how important layer nano-structure is in determining the hardness, coherence, and stress properties of a coating layer - properties that are required to increase the mechanical durability of a surface [see: Engineering Hard Durable Coatings" in CMN V18 I2, June 2008) and references 1]. A film layer structured as nano-crystalline units containing open pores, often in the form of columns, is permeable to the deep infusion of water vapor. When exposed to moist atmospheres, diffused water reacts to form hydrated surfaces thereby reducing the bond strengths that existed before contamination. The result is softening of the layer and reduction of mechanical strength. In some cases, detrimental changes in internal stress level are created. Deposition processes and material preparation are developed with the specific goal of growing dense nanostructure with low intrinsic stress. In principle, film layers that possesses these characteristics and are insoluble should resist the effects of water on their optical and mechanical properties. In fact, studies have revealed the influence of water on reducing the wear resistance of oxides and ceramics (see references in 1). Exposure reduces the hardness and increases the fracture resistance of such coatings and makes them susceptible to plastic deformation when the film is scratched [2].

The study reported in reference 1 is relevant to protecting multi-layer solar control coatings that are used on architectural glass, and provides some insight into the mechanical consequences. Solar heating control stacks built by magnetron sputtering were studied. Their composition is: glass/ TiO_2/ ZnO/ 10 nm Ag /ITO /SnO_2 / TiO_2 to a total thickness of ~100 nm. In addition to testing the full stack, single layers 400 nm thick of TiO_2, ZnO, and SnO_2 were tested. The mechanical hardness and nanoindentation load displacement were measured for coatings that were dry, were soaked in methylated spirit, and soaked in water for 1 hour and for 24 hours. No significant softening appeared for the full stack with the non-aqueous soak or the 1 hour water soak. The full stack showed significant displacement between dry and 24 hours wet

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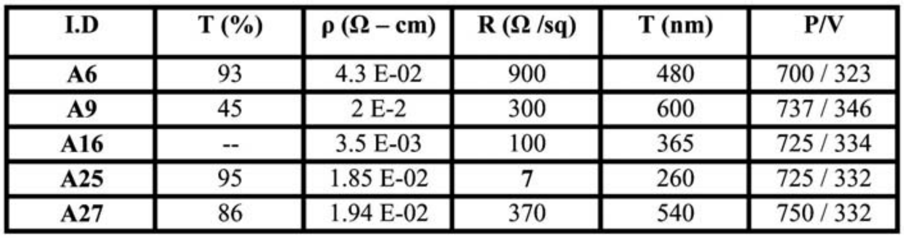
at large loads (10 to 500 mN), but reducing the load revealed that a soft, thin layer had been created by the 24 hours water soak. Fracturing caused by the indenter permitted water and atmospheric gases to reach and react with inner layers including silver. Work was then directed toward individual layers to determine which oxide provides the most durable protection.

Testing of the individual layers revealed their chemomechanical effects. Greater indenter displacement is experienced for the TiO_2 layer after 24 hours soaking compared to a dry layer. Low loading <10 mN) again revealed the creation of a soft layer of reacted material whose hardness is reduced from ~10 GPa to ~9 GPa. The ZnO layer experienced a similar indenter displacement, but a larger reduction in hardness with load. The SnO_2 layer showed little effect. SnO_2 is used to protect glass bottles from scratching even after washing, so is known to retain its hardness properties. TiO_2 and ZnO layers, in contrast, do not retain their mechanical properties after extended exposure to water. The results of the published study suggest that other oxides or denser layer nano-structures are needed to prevent water-induced softening of layers intended for surface protection.

Table 1



I.D	T (%)	ρ (Ω – cm)	R (Ω /sq)	T (nm)	P/V
A6	93	4.3 E-02	900	480	700 / 323
A9	45	2 E-2	300	600	737 / 346
A16	--	3.5 E-03	100	365	725 / 334
A25	95	1.85 E-02	**7**	260	725 / 332
A27	86	1.94 E-02	370	540	750 / 332

What Happens to Stress and Optical Properties when TiO_2 Films are Annealed?

Titania is a favorite material for visible-range coatings because of its high refractive index and because many dozens of deposition-related papers have appeared that teach the optimum processes for producing good films with reasonable ease. Titania is mostly used in AR coatings for ophthalmic, instrument panel, and architectural window coatings. Past CMN issues have discussed this material, its starting material forms and proper pre-evaporation conditioning, and its optical properties.

A recent study of the deposition process-dependent stress and optical properties has been reported [3]. The deposition processes for the films were: E-beam with IAD (EIAD), RF ion-beam sputtering with IAD, and DC magnetron sputtering with IAD. The researchers studied the effect of thermal annealing in air on stress, n and k, and roughness after exposure in 50 C° temperature steps from 100° C to 300° C. EIAD started with Ti_3O_5, the recommended source composition; the sputter targets were 99.99% Ti metal. An important parameter missing from the publication is the temperature of the substrate during film growth. The EIAD film showed the lowest compressive stress (-37 MPa) and little dependence on annealing temperature. The DC sputtered film had the highest (-886 MPa) that decreased to -500 MPa after annealing at 250° C. The RF sputtered film started at -527 MPa and decreased to -400 at 250° C. The DC film showed the highest index and extinction coef. (4 E-03); the *n*-values showed little dependence on annealing temperature. The *k*-values were essentially constant with anneal except for the EIAD film whose *k* increased from 0 to 7 E-03 at 200° C and then returned to 0 at 300° C. The *k* for the RF film was ~1.5 E-03. The EIAD exhibited greater surface roughness (~0.9 nm) compared with the DC film (~0.6 nm), while the RF film was ~0.8 nm. XRD showed a transition of the EIAD film from amorphous to anatase phase at 300° C, while the sputtered films had a stable morphology. This explains the roughness of the EIAD film.

The conclusions are: thermal annealing reduced the higher stress of the sputtered films compared with the low initial stress of the EIAD film. Little if any effect on index was experienced. The EIAD film's *k* value changed from very low to high, and then back to very low as annealing temperature was increased. Sputtering with assisted ion bombardment seems to produce TiO_2 films of greater crystalline stability than E-beam with IAD.

AZO TCOs for CIGS Solar Cell Applications

Al doped ZnO (AZO) is becoming popular as a transparent conducting oxide (TCO) replacement for ITO. We have discussed the economic and transparency advantages of AZO previously [4]. Applications of this TCO include the front transparent window and contact on thin-film amorphous silicon and CuInGaSe (CIGS) solar cells. AZO is also used in gas sensing and surface acoustic wave (SAW) devices and UV emitters. The favored deposition process is DC reactive magnetron sputtering of Al:doped ZnO targets, and Al_2O_3/ZnO targets are used with RF sputtering. In the recent report reviewed here, a target 99.9% pure Zn alloyed with 2% (m/m) Al was used [5]. The researchers deposited films using O_2 gas flow and target voltage settings that occur within the hysteresis transition region, O_2 flows 20-45 sccm and voltage drop 325 – 600 V. To overcome the instability of such operation, plasma emission was used to control the gas flow by monitoring the metal emission line. A set of transparency and resistivity values was determined at different voltage settings and nearly constant power. The table lists some examples of transparency (transmittance average from 450 – 500 nm) and resistance. Close examination shows large variations in resistance occur with small changes in power and voltage, suggesting a strong relationship with voltage. Sample A25 has a sheet resistance of 7 Ω /sq for a thickness of 260 nm, yet the P and V values are not substantially different compared to the other tests, making this result exceptional. Perhaps another sensitive parameter or two must have been encountered to achieve this low R. The resistance of the other high transmittance samples ranges from 300 to 900 Ω /sq for thicknesses 500 – 600 nm.

Spectroscopic ellipsometry (SE) modeling to determine the absorption coefficients of these samples suggested a positive correlation relating smaller absorption with lower resistance. The other conclusion that can be drawn is that oxygen and voltage deposition parameters for producing low sheet resistances with AZO are very critical; and from experience, we can conclude that this sensitivity is greater than that for ITO deposition.

Obtaining resistivity and transmission >80% with AZO (and ZnO-based materials in general) that is as low as that obtained with ITO is proving to be difficult, independent of the deposition technique used. A recent paper demonstrates the advantages of the sputtering technique variation, high power pulsed magnetron sputtering (HPPMS), to achieve 37 Ω /sq sheet resistance with 150 nm thick AZO films on 200° C substrates. The best obtained using reactive DC magnetron sputtering (RDCMS) was 50 Ω /sq [6]. ITO films of thickness ~500 nm deposited on 300° C substrates by both HPPMS and RDCMS gave about the same resistance, <3 Ω /sq, and ~85% transmission. On unheated substrates, the resistivity is 10 X higher. Process control based on plasma emission was able to stabilize the discharge in the transition mode, and this seems to be the process needed to achieve the minimum resistivity for AZO and similar compositions. Voltage and O_2 flow rate have large influences on film roughness (scatter) and resistivity, and the reader is encouraged to consult the paper for details.

CERAC is developing AZO target compositions with varied Al doping concentrations to produce films with lower sheet resistance, and parallel efforts are being directed toward deposition process optimization. Stay tuned to these pages for future reports.

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