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Coating Materials News

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In This Issue

The latest results of optical coating development were presented by researchers at the international Optical Interference Conference held in Tucson, June 6-11. Sub-disciplines: coating techniques, laser damage studies, film stress management, materials properties, tailored nano-structures, solar coatings, polarization, monitoring, measurements, manufacturing, and ultra fast coatings were discussed. We summarize some papers that have interest for our readership. A future issue of Applied Optics will contain full articles of the contributed conference papers.

Contents

Alternative Transparent Conducting Coatings

Metal oxides, doped and un-doped, can be made conducting and transparent in a reducing atmosphere such as hydrogen at high temperature. Indeed, resistance can be modified by post deposition annealing either in hydrogen or vacuum. At temperatures near 400° C atomic hydrogen becomes available to metal cations and provides free carriers in the oxide lattice defect states near the conduction band minimum as a result of the formation of oxygen vacancies generated with the release of water. For conditions when reduction reaction does not occur but rather the hydrogen is incorporated interstitially, the hydrogen can act as a shallow donor for *n*-type conduction. *N*-type conducting films of ZnO containing H_2 can be generated by sputtering in a hydrogen atmosphere, exposure to a H plasma, and by ion beam irradiation [1].

In addition to their application to displays, OLEDs, LCDs, etc, TCOs are used as the transparent electrode in solar cells. Required properties are >85% high visible transparency and low resistivity (<10 E-3 Ω-cm). Recall that:

> Sheet resistance Ω/□ = ρ(Ω-cm) x 10^7 /t (nm), where ρ is resistivity and t is film thickness.

We have previously discussed the need to develop alternatives to ITO TCOs for economic, supply, and environmental stability reasons [2]. In the solar cell production process, ITO exhibits instability of properties to a hydrogen plasma process step. One alternative material set is that based on doped Zinc Oxide. A further requirement is application to polymer substrates that have a low temperature limitation. AZO, Aluminum: Zinc Oxide, and GZO, Gallium: ZnO, are receiving attention for their advantages compared to ITO.

Attempts to evaporate AZO compositions and achieve low sheet resistance have met with difficulty; therefore the favored technique is DC magnetron sputtering from doped targets. For CIGS solar cells, sputtering of AZO is combined with chemical deposition to build stacks consisting of conduction and buffer layers.

Researchers at Thin Film Technology Center /Department of Optics and Photonics, National Central University, Chung-Li, 320, Taiwan investigated the influence of Hydrogen flow rate during pulsed DC magnetron sputtering [3]. Power was 200 W and frequency 100 kH. The sputtering targets were ZnO mixed with 2 wt % Al_2O_3 and ZnO mixed with 4 wt.% Ga_2O_3 powders. H_2 flow rates were varied from 2 to 20 sccm. Sputtering permitted films to be grown at temperatures near 100° C. It was found that the carrier concentration and mobility were increased as the H_2 flow was increased from 1 to 5-10 sccm, resulting in lower resistivity and higher transmission. Resistivity near 10E-04 Ω-cm was achieved. This is a significant improvement over previous attempts to grow ZO films at low substrate temperature. Incorporation of H_2 causes high doping efficiency and electron carrier concentration.

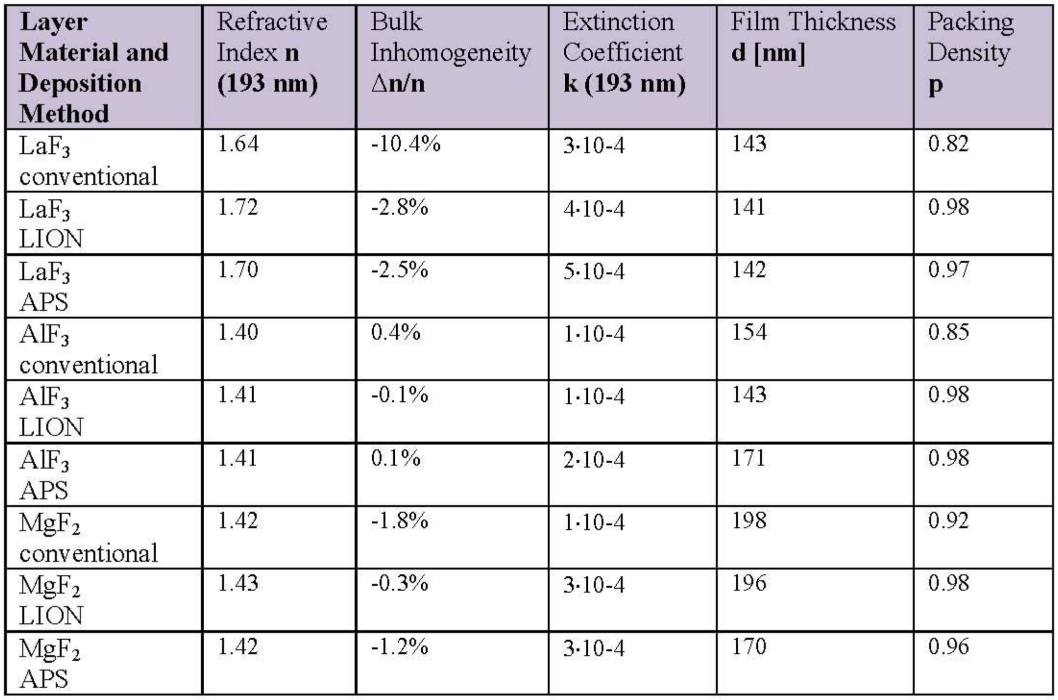
Another study reported used E-beam evaporation with IAD, introducing varied concentrations of oxygen and IAD energy to change crystallinity and optical and

continued on page 2

Fluoride Compounds Deposited Using Plasma Ion Techniques

Photolithographic projection systems for patterning structures using the ArF 193 nm laser can only use fluoride coatings because at this UV wavelength all oxide materials absorb. The materials useable are MgF_2 and AlF_3 for low index and LaF_3 for high index layers. Layers of fluoride compounds typically grow with a columnar nano-structure, and only moderate packing density is achieved at temperatures even as high as 300° C. Conventional practice is to use a Ta boat in resistance-heated evaporation because most fluoride compounds melt at a relatively low temperature compared with oxide compounds. Electron-beam evaporation sources were found to produce superior fluoride films compared to resistance heated (RH) boat sources [5]. Greater densification without the introduction of substantial UV absorption can be achieved using plasma-assisted techniques such as PIAD (APS) or Leybold's LION process. Plasma processes are not compatible with RH because of arcing. Films deposited without plasma assistance have a low packing density, low refractive index, higher surface roughness, and are inhomogeneous. We reproduce the tabulated results from that paper for the three fluoride compounds deposited without and with the two plasma processes [6]. It can be seen that the energetic plasma processes produce films with higher packing density and index, low extinction coefficients and better homogeneity.

Table 1



Layer Material and Deposition Method	Refractive Index **n (193 nm)**	Bulk Inhomogeneity **Δn/n**	Extinction Coefficient **k (193 nm)**	Film Thickness **d [nm]**	Packing Density **p**
LaF_3 conventional	1.64	-10.4%	3·10-4	143	0.82
LaF_3 LION	1.72	-2.8%	4·10-4	141	0.98
LaF_3 APS	1.70	-2.5%	5·10-4	142	0.97
AlF_3 conventional	1.40	0.4%	1·10-4	154	0.85
AlF_3 LION	1.41	-0.1%	1·10-4	143	0.98
AlF_3 APS	1.41	0.1%	2·10-4	171	0.98
MgF_2 conventional	1.42	-1.8%	1·10-4	198	0.92
MgF_2 LION	1.43	-0.3%	3·10-4	196	0.98
MgF_2 APS	1.42	-1.2%	3·10-4	170	0.96

Table 1. Results from spectral photometry and FTIR measurement: optical constants (n, k), bulk inhomogeneity (Δn/n), film thickness, and packing density. The MeF single layers were deposited conventionally and with the assistance of the LION plasma source and the APS. Substrate was Suprasil 2. (From Ref [6]).

"Alternative Transparent Conducting Coatings" ***from page 1***

electrical properties. The minimum resistivity with good transparency that was achieved for ~100° C was ~0.06 Ω-cm. An Oxygen / Argon ratio of 1:2 was used and partial pressures were varied between 4×E-4 and 6×10-4 Torr. The IAD power beam current, beam voltage 100 V and the acceleration voltage were varied. High energy produced more defects and higher conduction. Oxygen partial pressure affected the crystallinity and optical properties [4].

Laser Coatings

Papers were presented by workers in the high energy laser community. For inertial confinement systems such as the Omega project of the Laboratory for Laser Energetics, hafnia and silica multilayers are used for high reflector and AR coatings that operate at 351 and 1053 nm. This combination evaporated by E-beam provides coatings with high laser damage resistance with high tensile stress especially on fused silica substrates in low relative-humidity environments. Substrate deformation and crazing of the coating are frequent problems. In this work [7], the use of aluminum oxide is explored as a means of creating a more compressive stress in multilayer reflective coatings. Stress in hafnia/silica multilayers typically starts out as compressive and evolves to tensive. The desirable state is a low value of compressive to avoid the possibility of tensile cracking that would greatly lower the laser damage threshold.

A persistent problem with such coatings is their long-term shift in stress properties, especially in a vacuum environment. In the previous quarter's issue of CMN, we discussed SiO_2 deposition and the instability of stress as related to the ambient humidity. It was mentioned that the addition of small percentages of alumina to the silica layer results in increased packing density and can produce lower tensive stress. In a reported effort, alumina layers inserted within oxide multilayer stacks contributed compressive stress that helped to counterbalance tensive stress [7]. The researchers succeeded in reducing the overall level of tensive stress of the reflector designs. The mechanism that resulted in the reduction of stress is not clear since single layers of alumina exhibit large tensive stress.

Long-term Stress in Silica Coatings

Silica coatings were discussed in last quarter's issue. As mentioned above, there is a troublesome change in stress level over periods of months that exhibits not only changes in optical properties, but also changes in mechanical properties. In the extreme case, films have been known to peel from some substrate materials. The compressive stress gradually is observed to reduce with time. A study employing conventional E-beam deposition and E-beam + IAD showed greater changes in stress over time for E-beam than with IAD of increasing power [8]. E-beam films showed a reduction in compressive stress, and the IAD films showed an increase. The E-beam films changed in stress level from 400 MPa to 200 MPa, while the IAD films changed from 200 MPa to 300 or from 300 MPA to 400 MPa depending on the IAD power. Higher power induced greater initial stress, and smaller change with time. The authors used the Si-OH absorption band near 930 cm-1 as related to stress evolution, and concluded that a chemical reaction is responsible for the temporal change.

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