Bipolar Pulsed DC Sputtering of Optical Films

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ABSTRACT

Bipolar pulsed DC sputtering is a new technique for high rate reactive deposition of dielectric oxides on diverse types of substrates. This effort reports on the application of Bipolar pulsed DC sputtering to generate single layer and multilayer oxide coatings on flat, curved, glass and plastic substrate surfaces. The optical (refractive index and extinction coefficient) and physical (durability and moisture stability) properties of Ta_2O_5 TiO_2, ZrO_2, Nb_2O_5, WO_4, Al_2O_3 and SiO_2 films and film stacks are presented.

INTRODUCTION

The production of thin film dielectric coatings for precision optics and ophthalmic applications has long been dominated by evaporative techniques. Resistance and electron beam deposition sources, alone or in tandem with energetic ion sources (to facilitate substrate precleaning and/or modify the properties of a growing film) have been implemented in thousands of systems worldwide. The long throw distances required for evaporation have been indirectly very useful at producing uniform coatings over the curved surfaces found on the bulk of the optics processed through these systems. Coupled with modern controls and automation, evaporative systems offer a robust production solution to many optical thin film requirements.

The components and subsystems required to manufacture a modern evaporative coating system are available in a limited size and performance range. Automation, instrumentation and controls can be considered fixed costs for they do not vary substantively with system size, and generally account for the lion's share of the total system costs. These two phenomena yield a cost and capacity inversion. In general, modern evaporative system capacity scales geometrically with the system price.

Although this argument delights the modern deposition system manufacturer, the converse has significant economic implications. As price is reduced, the capacity roll off is so severe that a discernable lower limit in system size is reached. Currently, this value is approximately 250 k$(USD) for a modern evaporator with an internal volume exceeding 175 l, generous pumping speed (> 1500 l/sec air speed) and capable of executing ion beam assisted deposition (IBAD). There do not appear to be any significant technical breakthroughs on the horizon to significantly lower this cost.

The downward "push" on deposition system manufacturers to deliver high performance optical coatings from small, simple systems has heightened over the past few years. In addition, the performance "bar", particularly film density and its' role towards minimizing spectral shifts due to water uptake, has been raised. Average lot sizes have gone down and the production of optical coatings is now being transitioned into technically unsophisticated environments. These criteria have driven the development of sputtering technologies that promise, in very specific applications, to be successful.

Techniques for reactively sputtering dielectrics have been extensively reported in the open literature. In general, RF reactive sputtering is easy to implement and successful with a wide range of nitrides and oxides [1-7]. However this technique exhibits such a low deposition rate and high heat load (due to a significant electron flux at the substrate interface) that it is generally considered to have limited commercial importance. DC/AC reactive sputtering typically exhibits order of magnitude greater deposition rates than RF techniques [8-13]. However, target "poisoning", the criticality of a well defined anode and the metastable nature of the process has generally restricted DC reactive deposition to narrow, high volume (and high system cost) applications (architectural glass, packaging, etc.).

Over the past few years significant developments in sputtering power supplies and a refined understanding of the role that magnetic and electric field profiles/distribution play in reactive sputtering technology have lead to truly breakthrough technologies.

Asymmetric Bipolar Pulsed DC [14-17] has arrived as an enabling technology for the production of dielectric coatings for optical applications. This technique is based on the addition of a reverse voltage bias pulse to the normal DC waveform. This bias pulse, implemented at a frequency

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high enough to exploit the mobility differences between ions and electrons in plasma, accentuates the sputtering of dielectric films which accumulate on the target surface and effectively eliminates target poisoning and arcing. Pulse frequency and duty cycle can be varied to optimize the process for a specific cathode target material and ultimately, the relevant optical properties of the deposited films. This technique is particularly attractive because it can be implemented on a single cathode and consequently, delivered in small profile systems.

This paper reports on the application of Asymmetric Bipolar Pulsed DC to the generation of single and multi-layer oxide coatings for optical interference coatings. Ta_2O_5, TiO_2, ZrO_2, Nb_2O_5, WO_3 Al_2O_3, and SiO_2 films were generated using this technique. A parametric study of the resultant optical (refractive index and extinction coefficient) and physical (durability and moisture stability) properties of single films and multi-layer optical designs as a function of processing conditions is presented.

DISCRIPTION OF EQUIPMENT

All thin films and optical stacks were generated in a Denton Vacuum Discovery® 18 sputtering system. The Discovery® 18 used for this evaluation was equipped with a loadlock and three, 3.0" diameter, DVI planar magnetron sputter sources (Figure 1). Substrates were positioned in the main chamber (65-liter internal volume) on a rotating substrate stage (150 mm in diameter) which although biasable, was

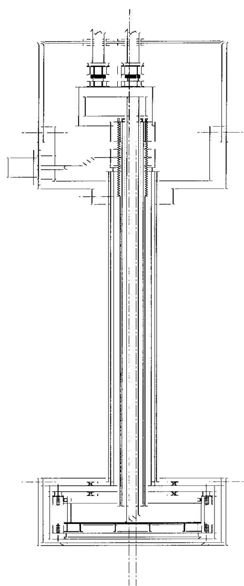

Figure 1. Cross sectional view of DVI planar magnetron sputter source.

permitted to float to plasma potential (V_p) for the course of this evaluation. The chamber was pumped with a 145-l/sec turbomolecular pump with a measured effective speed in the deposition chamber of 65 l/sec.

Process gases were introduced into the system by two mass flow controllers (MKS Instruments model 2179) which fed a common mixing manifold upstream of the main chamber injection port. All reported process pressure measures were made with a capacitance manometer (MKS model 628A, 0.1 torr full scale, and 100°C internal temperature regulation).

The planar magnetrons were inclined 30° from normal; with their centerline impinging the rotating sample stage 25 mm off-axis from the center of rotation (Figure 2). This "confocal" cathode orientation has been empirically demonstrated to yields a thickness non-uniformity of < 3.0% over the 150 mm substrate diameter. All targets were clamped to the cathode backing plates with the exception of Si which was metallic solder-bonded. An air-actuated shutter allowed the targets to be conditioned before the films were deposited on the substrates. An ENI RPK-50 (5.0 kW) Asymmetric Bipolar Pulsed DC power supply was used to drive the magnetrons.

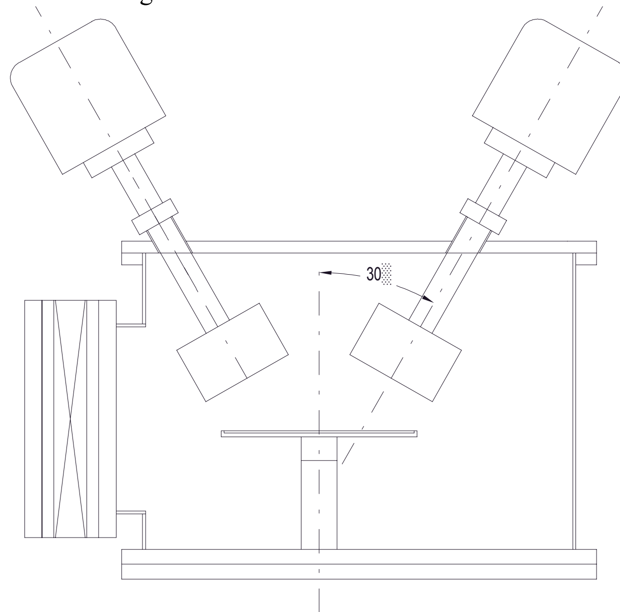

Figure 2. DVI D-18 general system arrangement.

EXPERIMENTAL TECHNIQUES

All of the samples for this study were clear or frosted microscope slides and 2" diameter silicon wafers used for stress measurements. Samples were cleaned using an alcohol wipe, attached to a substrate platen with kapton tape and blown off with dry argon using an anti-static gun. The samples were inserted into the main chamber through a loadlock so that the sputter targets were not exposed to atmosphere between runs. The deposition chamber was allowed to pump into the mid 10^{-7} mTorr range before starting all depositions. All depositions were started at

ambient temperature. O_2 and Ar were introduced at flows to achieve the desired total pressure (ranging from 7.5 mTorr to 15 mTorr) and gas mixtures (% O_2). Power settings ranging from 350 to 700 watts were used. The power supply was turned on with the target shuttered and the frequency and pulse width were adjusted to give a duty cycle (DC) of approximately 40%. The shutter was opened after conditioning the target for 30 sec.

Transmittance and reflectance scans were used to determine the optical properties and moisture stability of the films, as reported previously [18]. Stress measurements and calculations were made using a model 128 tool made by Frontier Semiconductor Measurements, Inc.

RESULTS

Ta_2O_5, TiO_2, ZrO_2, Nb_2O_5, WO_3 Al_2O_3, and SiO_2 were evaluated; those materials where parameters for which reasonably high rates were discovered, were studied in more depth. Those materials that did not exhibit high deposition rates were subjected to a cursory examination and will be evaluated in greater detail at a later date. Three materials fell into this latter group exhibiting deposition rates of approximately 1± Å/sec. They were Al_2O_3 (n ~ 1.60), TiO_2 (n ~ 2.45) and ZrO_2 (n ~ 2.15). These refractive indexes are close to what was expected except for the Al_2O_3, which was lower than expected.

The pp (partial pressure) O_2 level required to make good optical films from the various target materials was dependent on the material, the sputtering rates from the target and the power levels. Basically SiO_2 (1.5-2.25 mTorr) and the Nb_2O_5 (1.5-2.5 mTorr) required the lowest oxygen partial pressure, while the Ta_2O_5 (1.5-3.0 mTorr) required higher levels and WO_3 (3.0-5.0 mTorr) needed the most. The lower values were for 350 watts power and the

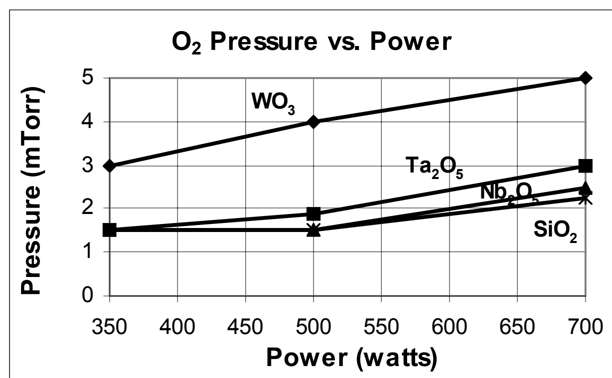

Figure 3. Minimum pressure levels vs. power required for clear non-absorbing optical films.

higher values were for 700 watts power (see figure 3). Each line represents the lowest pp of O_2 which produced an optically non-absorbing film of the oxide. Lower pp O_2 levels resulted in a highly absorbing and/or metallic film (except for WO_3 where absorbing cobalt blue films were possible).

SiO_2 was deposited from a silicon (99.999%) target bonded to a backing plate. The deposition rates data are shown in figure 4 and the refractive indexes at 560 nm in figure 5. These refractive indexes were a little lower than we had expected and none of the films were moisture stable.

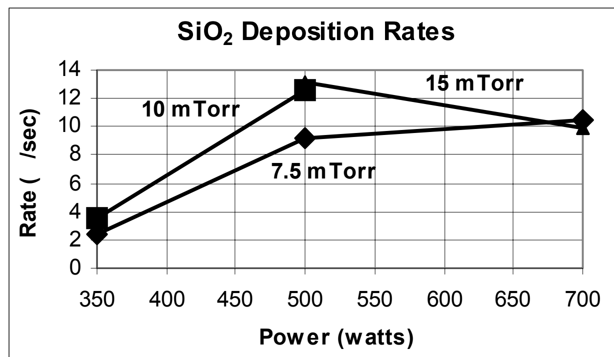

Figure 4. Deposition rates vs. power and total pressure for SiO_2.

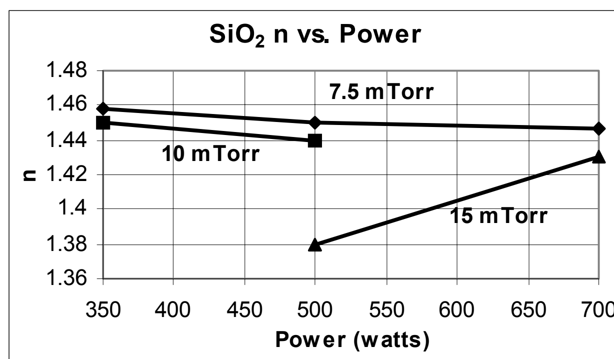

Figure 5. n vs. power and total pressure for SiO_2.

Ta_2O_5 was deposited from a pure tantalum (99.5%) target clamped to the cathode plate. The deposition rates are shown in Figure 6 for various power levels and the refractive indexes at 560 nm in figure 7. These refractive indexes are a little lower than those obtained from IAD electron beam evaporated films, however they were moisture stable.

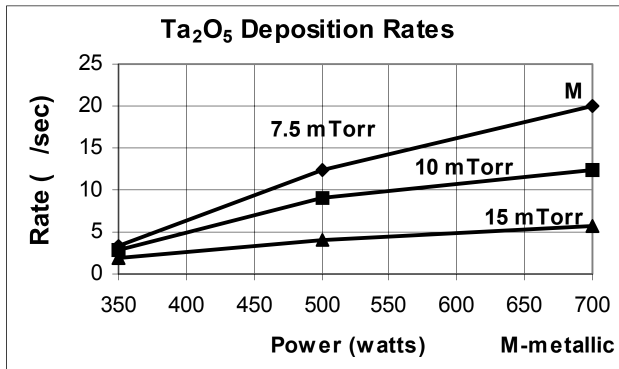

Figure 6. Deposition rates vs. power and total pressure for Ta_2O_5.

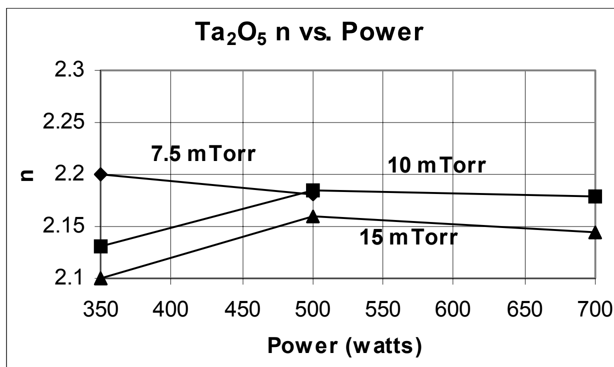

Figure 7. n (560 nm) vs. power/total pressure for Ta_2O_5.

Nb_2O_5 was deposited from a pure niboium (99.95%) target clamped to the cathode plate. The deposition rates are shown in Figure 8 for various power levels and the refractive indexes at 560 nm in figure 9. These refractive indexes are a little lower than those obtained from IAD evaporated films, however they were moisture stable.

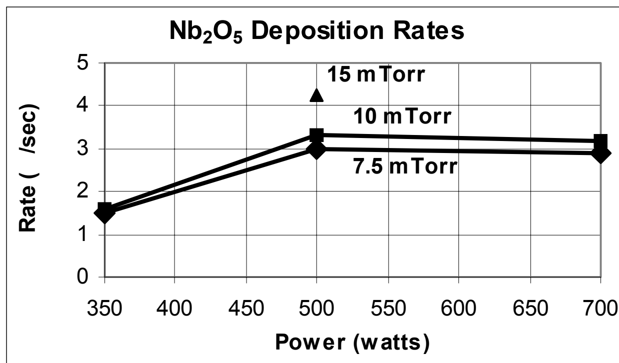

Figure 8. Deposition rates vs. power and total pressure for Nb_2O_5.

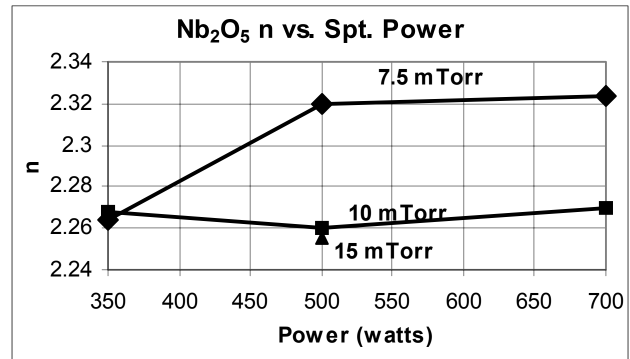

Figure 9. n (560 nm) vs. power/total pressure for Ta_2O_5.

WO_3 was deposited from a pure tungsten (99.95%) target clamped to the cathode plate. The deposition rates are shown in Figure 10 for various power levels and the refractive indexes at 560 nm in figure 11. These refractive indexes were somewhat lower than we had expected, however the films were moisture stable. The interesting thing about the WO_3 films was the relative ease in getting very high rate depositions. Also, the absorbing films were typically blue in color. This color is due to the electrochromic nature of WO_3 and has been explained by Bishop, et. al. [19].

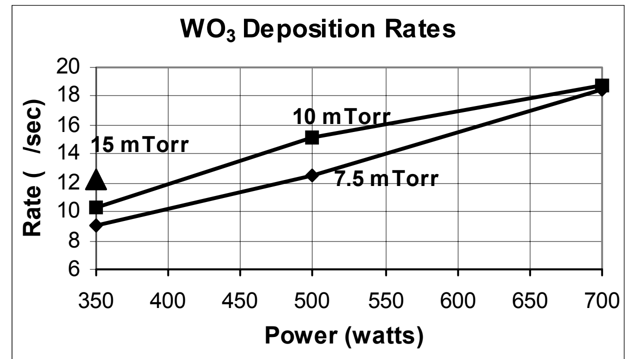

Figure 10. Deposition rates vs. power and total pressure for WO_3.

The refractive indexes for the high index materials shown in figures 7,9 and 11 are at a wavelength of 560 nm. The dispersive refractive index of the films was determined over the 350 nm to 2000 nm wavelength range. Each material had traditional dispersion as shown (400 nm to 1000 nm) in figure 12. The index shown is the medium index for the material. The index range observed was ± .05 for Ta_2O_5, ±.04 for Nb_2O_5 and ± .02 for WO_3.

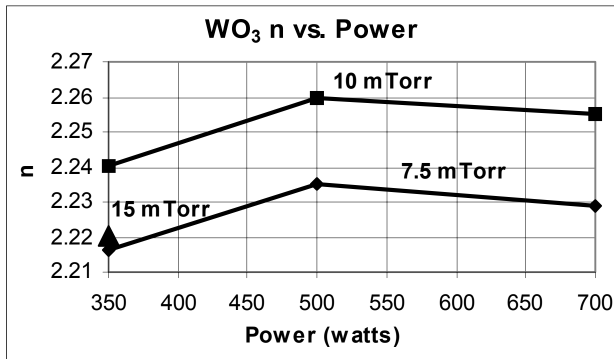

Figure 11. n (560 nm) vs. power/total pressure for WO_3.

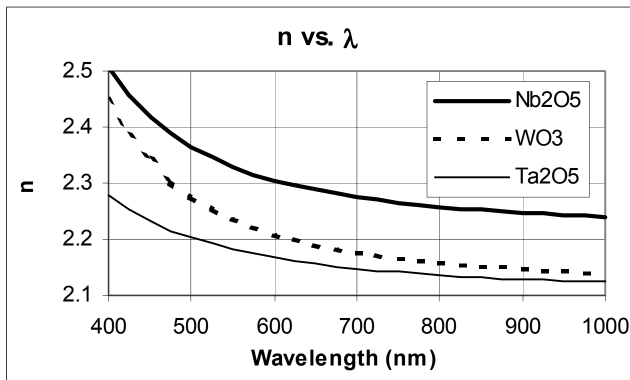

Figure 12. Dispersion curves for medium refractive index of 3 high index materials.

STRESS MEASUREMENTS

Deposition parameters for each of the film materials were selected and used to deposit ~4000 Å of material on previously characterized 2" silicon slides. The change in the curvature of the slices was then use to calculate the stress between the film and the substrate. The measured stress data is recorded in figures 13–16. Negative values indicate compressive stress and positive values indicate tensile stress. All films become more tensile as the sputtering pressure increases. SiO_2, Ta_2O_5 and Nb_2O_5 are compressive and become more tensile as the power is increased. The WO_3 is slightly tensile at lower power levels becomes more compressive as the power is increased (and becoming very compressive at 700 watts).

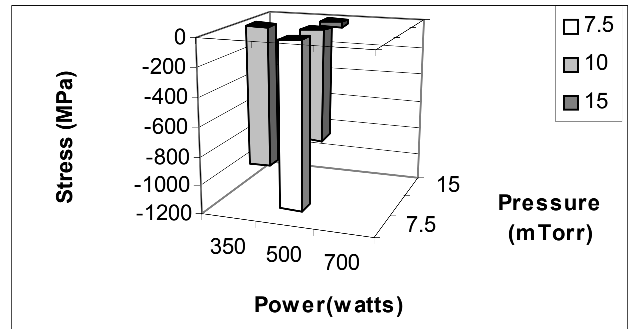

Figure 13. SiO_2 stress data

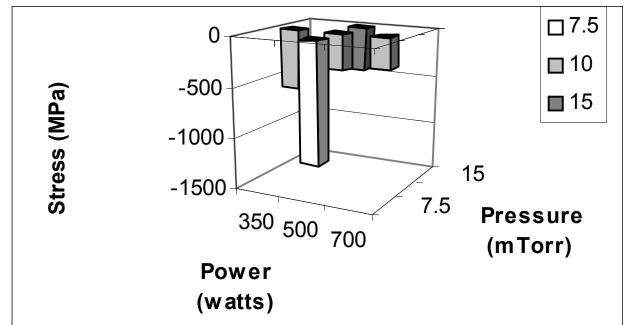

Figure 14. Ta_2O_5 stress data.

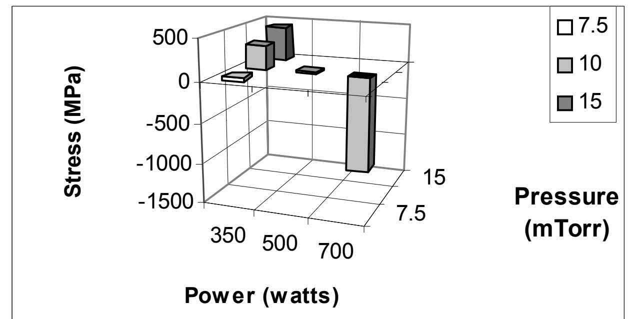

Figure 15. WO_3 stress data.

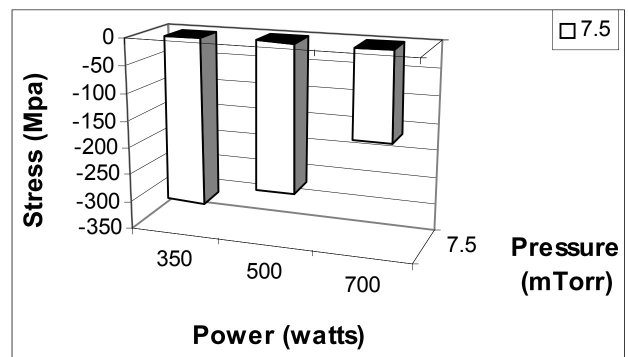

Figure 16. Nb_2O_5 stress data.

EXAMPLE FILM DESIGNS

As previously stated a primary reason for this study was the opportunity to fabricate certain multi-layer film structures in a lower volume, low cost coating system. Therefore, after the initial characterization of the Ta_2O_5/SiO_2 films, a multilayer AR was designed and deposited on the concave and convex sides of polycarbonate lenses. Flat witness samples were located on the tooling to approximate the level of the apex of the lenses in order to approximate the spectral performance of the lenses. A typical example of this coating is shown in figure 17. The unedged lens blanks have the traditional green color over most of the surface with a tendency to red around the outer edge. The finished lenses have the traditional green color. Samples of the lenses were subjected to durability measurements. The results were similar to those normally obtained from evaporated coatings.

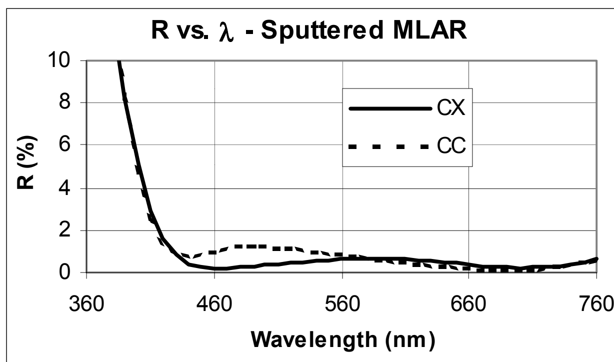

Figure 17. Spectral performance from flat witness samples for films deposited on convex (CX) and concave (CC) side of –2 lens surface.

We also fabricated a 12 layer reflector stack similar to what had been reported previously [18] for an E-gun evaporated coating. This coating was not moisture stable due to the SiO_2. Calculations for the refractive index ratio supports the index data reported in figures 5 and 7.

CONCLUSIONS

We have established that asymmetrically pulsed DC sputtering is a viable alternative to evaporated coatings for some low volume applications. Data obtained from the testing for the prototype system used for this study is the basis for designing specifically structured system for certain applications. Further work is planned for extending the study to additional materials and applications.

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