

Measurement and Correlation of Ion Beam Current Density to Moisture Stability of Oxide Film Stacks Fabricated by Cold Cathode Ion Assisted Deposition.

Dale E. Morton and Vitaly Fridman, Denton Vacuum, LLC., Moorestown, New Jersey, USA

Keywords: *Ion Beam Assisted Deposition, Ion Sources, Index of refraction of TiO₂, Optical film characterization*

ABSTRACT Durable and dense dielectric optical stacks, deposited with the assist of a gridded, Kaufman-type ion source have been extensively reported upon. A primary limitation of this technique is a significant reduction of ion source lifetime when high levels of oxygen are required to achieve specific film properties. Cold cathode ion sources, which are capable of continuous operation with 100% oxygen, have traditionally been used in a high current/low energy mode to assist in the fabrication of low absorption, high index oxide films. This work reports on the use of the cold cathode ion source at high energy levels to generate moisture stable thin film optical stacks. The optical properties and moisture stability of optical film stacks made from these oxides are presented as a function of the cold cathode ion source's operational parameters and the measured ion current density at the surface of the deposited films.

INTRODUCTION Considerable data has been generated and reported on the use of ion sources(1) for both substrate pre-cleaning and assisting in the deposition and growth processes of thin films (IAD) over the last 15 years. (2,3,4) There is now a plethora of ion sources available for commercial use as well as many "improvements" on the older designs. It has been well established that ion assisted deposition (IAD) modifies many of the optical and physical characteristics of thin films used for interference coatings. The parameter space of IAD is quite large and it is possible to degrade the deposited film's optical properties if the incorrect operating conditions are chosen. Ta₂O₅, TiO₂, Nb₂O₅ coatings, deposited on low temperature substrates using a high-current, low-voltage, ion source are the basis of this study. The optical characteristics (refractive index and absorption), moisture shift and abrasion resistance of the films (with/without IAD) are compared and contrasted. The ion sources were characterized and current density measurements made using the parameters which resulted in moisture stable films. Several film stacks of (HL)₆ design of various material combinations (Ta₂O₅/SiO₂, TiO₂/SiO₂, and Nb₂O₅/SiO₂) were deposited and measured.

EXPERIMENTAL METHOD This study was conducted in an Integrity[®]-29 (I-29) fully automated ophthalmic Cryo-pumped coating chamber equipped with resistive sources, a 6-pocket E-gun, quartz crystal rate/thickness controller, 3 kW quartz lamp heater and a cryogenically cooled Meissner surface. Internal fixturing consists of a domed calotte, a curved uniformity mask in front of the calotte which has a quartz crystal mounted in it, an electron beam-gun with the deposition pocket centered in the chamber and cold cathode ion sources (Denton Vacuum CC-104/105) 10 inches off-center position, pointing up and angled in towards the center of the calotte. The general equipment arrangement is shown in figure 1.

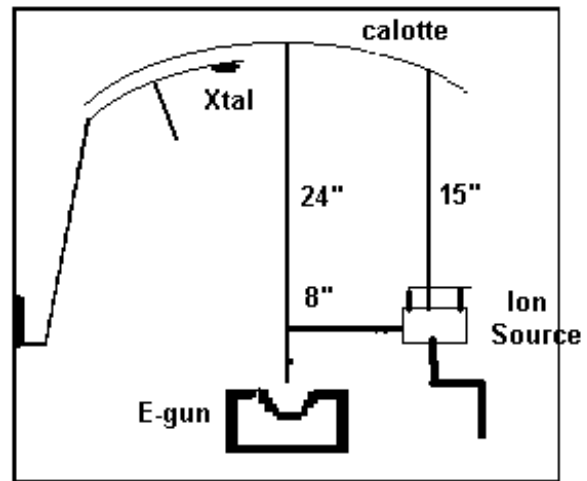


Figure 1. I-29 general equipment arrangement.

The ion sources were characterized two ways. First by using the general equipment arrangement and putting Faraday probes into the tooling around the outer radius as shown in figure 2. (simulating the surface of the parts during deposition) and second by tilting the ion sources straight up and placing the Faraday probes on a bar spacing them 5 cm apart and positioned 40 cm above the ion sources (traditional measurements taken for comparison purposes). Data was taken for O₂ flow rates ranging from 1x10⁻⁴ to 5x10⁻⁴ and for various ion source

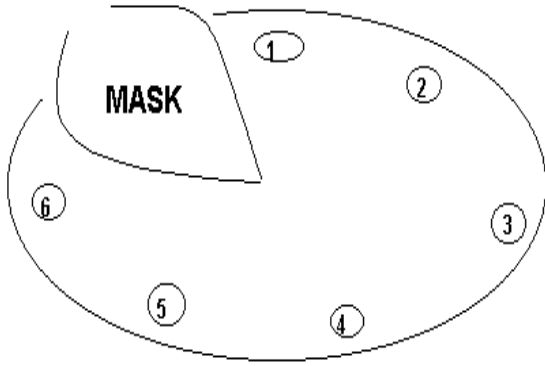


Figure 2. Faraday probes mounted in calotte. Position # 3 is directly above the ion source.

control parameters (neutralizer current and drive current). The ion current densities were then calculated.

The actual deposition process can cause variations in the ion current densities if the deposition process causes a variation in the parameters which affect the operation of the ion source. In particular, the gettering action of depositing a highly reactive material such as TiO_2 will reduce the pressure causing the drive voltage to increase in order to maintain drive current. Thus the ion current densities exposures for the various films deposited need to be deduced from the ion source parameters used for the characterization measurements and the control parameters used during the film deposition taking into account any variations caused by the deposition itself.

OPTICAL CHARACTERIZATION Spectral analysis consisted of measuring the transmittance of the clear samples and reflectance (at 6° incidence) of the frosted back samples. From this data the refractive index was calculated from the reflectance using:

$$n_\lambda = \left[n_s \cdot \frac{(1 \pm \sqrt{R_\lambda})}{(1 \mp \sqrt{R_\lambda})} \right]^{0.5} \quad (1)$$

where: n_λ is the refractive index at λ
 n_s is the refractive index of the substrate
 λ the wavelength for an odd order in the interference pattern
 R_λ Reflectance at λ

The extinction coefficient k_λ was calculated from the reflectance and the transmittance data using the following relationship given by Macleod(5):

$$k_\lambda = \frac{\lambda \cdot (1 - T_\lambda - R_\lambda)}{2\pi \cdot d_m \cdot \left(\frac{n_s^2 + n_f^2}{n_s \cdot n_f^2} \right)} \quad (2)$$

where T_λ has been corrected to first surface transmittance

Film thicknesses (d_m) were either measured directly using a stylus profilometer or were calculated from the interference pattern and the index of the materials using:

$$d_m = \frac{m \cdot \lambda}{4 \cdot n_\lambda} \quad (3)$$

where d_m is the thickness calculated at the m^{th} order in the interference pattern.

At wavelengths where the film is nonabsorbing, this calculation results in thickness which is within the accuracy of the measurements being made. Typically the calculated thickness was the same for each order in the interference pattern unless the film was absorbing. Thus the thickness calculation at all orders also became a good indicator of when the film was becoming absorbing.

If the film is absorbing, then the refractive index needs to be corrected using the relationship(5):

$$N_\lambda = n_\lambda + \left(\frac{\pi \cdot k_\lambda \cdot d}{\lambda} \right) \left(\frac{1 + \sqrt{R_\lambda}}{1 - \sqrt{R_\lambda}} - n_s \right) \quad (4)$$

where N_λ is the corrected refractive index and the conditions for determining the relationship are the same as for equation 2. However, in this case the thickness of the film calculated from a longer wavelength non-absorbing region is used.

The corrected refractive index data was then used to calculate a dispersion relationship of the following type to be used in comparing films prepared under varying conditions:

$$N_\lambda = A + \frac{B}{(\lambda - C)^2} \quad (5)$$

where A, B and C are coefficients determined for data over the visible spectral region.

MOISTURE STABILITY MEASUREMENT The moisture stability of the samples was determined by soaking the samples in water, scanning transmittance (reflectance scans could not be used since the Al mirrors in the reflectance attachment were moisture sensitive causing a reference change which would appear as an index change in the film), then drying them while in the spectrophotometer with a dry nitrogen purge and rescanning after 20 minutes. Typically, most of the moisture shift (>90%) would occur in the first 5 or 10 minutes of purging and there would be little or no further moisture shift in the next 10 minutes of purging. The moisture shift of the stacks was then measured and recorded both as a bandwidth (BW) change and as a change in the refractive index ratio for the materials.

ION CURRENT DENSITY MEASUREMENT RESULTS

Ion current density measurements were made using a set of 6 simple Faraday probes ordered around the outer edge of the single rotation calotte as shown in figure 2. These measurements closely simulates the largest range of current density flux to which the parts will be exposed during deposition. Preliminary results for films prepared on samples across the radius of the calotte showed little variation in optical properties but indicated that the samples about the outer edge were slightly lower in refractive index. Thus the outer edge had the least or worst case exposure to the ion flux. Measurements were made for the full range of control parameters which was used in preparing the IAD films. An example of the data obtained for a given neutralizer current for the probes is plotted in figure 3 for parameters shown in the figure caption.

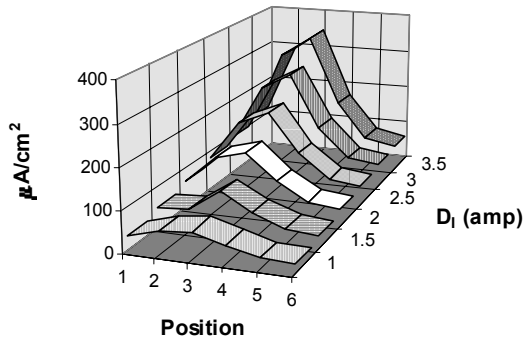


Figure 3. Ion current density measurements for Faraday probes mounted around a calotte (positions 1, 2, 3, 4, 5 and 6) for ion source drive current of 1, 1.5, 2, 2.5, 3 and 3.5 amps. O_2 flow was 28 sccm (2×10^{-4} Torr).

The parameters used in preparing the data for figure 4 are similar to those used in preparing a set of TiO_2 films for this study. However, during the deposition, the TiO_2 dissociates

and therefore getters oxygen when deposited on the substrates and throughout the chamber. This gettering action causes the pressure in the chamber to drop and the drive voltage required to maintain the desired drive current to increase. Therefore, it was necessary to simulate the vacuum conditions during deposition and take additional probe measurements to correlate the ion current densities during deposition of the various films.

A set of TiO_2 (titania) films were prepared at 40°C substrate temperature and $3.5 \text{ \AA}/\text{sec}$ with chamber pressures of approximately 1.6×10^{-4} Torr for drive currents ranging from 1 ampere to 3 ampere in 0.5 ampere increments. Spectral measurements were then made for these films and the moisture stability and optical properties determined.

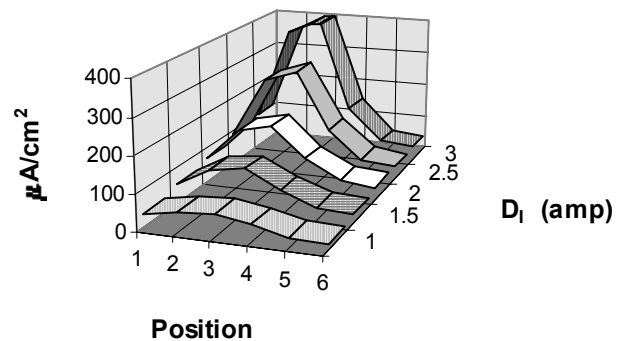


Figure 4. Ion current density measurements for Faraday probes mounted around a calotte (positions 1, 2, 3, 4, 5 and 6) for ion source drive current of 1, 1.5, 2, 2.5, 3 amps. O_2 flow was ~ 27 sccm (1.6×10^{-4} Torr).

The data for the current density simulation for these films is plotted in figure 4. This data was obtained by adjusting the O_2 flow rate to duplicate the pressure in the chamber during deposition and taking a set of current density measurements.

TiO_2 FILM DATA The results obtained for moisture stability and the optical characterization of the films is summarized in Table I. D_1 is the drive current during deposition of the films, CD_{avg} is the average current density ($\mu\text{A}/\text{cm}^2$) around the calotte, n_{560} is the refractive index at 560 nm, $k_{3\lambda/4}$ is the extinction coefficient at 560 nm and $\Delta n_{3\lambda/4}$ is the shift in the refractive index at the $3\lambda/4$ peak ($\sim 1000 \pm 50$ nm for all of the films) of the film. Δn is calculated from the change in the $3\lambda/4$ transmission peak. The films become progressively more moisture stable and the refractive index of the films increases as the current density exposure increases during deposition.

Table I.

#	D _I	CD _{avg}	n ₅₆₀	k ₅₆₀	Δn _{3λ/4}
non	0	0	2.201	0	-0.037
79	1.0	40	2.249	0.001	-0.036
80	1.5	69	2.280	0.0005	-0.029
82	2.0	101	2.328	0.0007	-0.023
87	2.5	145	2.349	<0.001	-0.003
85	3.0	187	2.488	<0.001	0

The refractive index profiles for the films shown in Table I are plotted in figure 5. The refractive indexes of the films increase as the drive current used for the IAD (and the current density exposure during deposition) increases. All of these films were prepared using as consistent conditions as possible, varying only the drive current to the ion source. Traditional techniques of controlling refractive indexes by varying pressure and/or deposition rate still prevail. That is, reducing the deposition rate while maintaining all other parameters will all cause the refractive index to increase and make a moisture stable film. This is shown in figure 4 by the dashed line for a film deposited more slowly (~2.5 Å/sec instead of 3.5 Å/sec) using a 2 amp drive current while maintaining all other parameters as before. The resultant refractive index and the moisture stability are comparable to the film prepared at the higher deposition rate and 3 amp drive current.

Basically we have found that moisture stable TiO₂ films have a refractive index of about 2.47 or higher at 560 nm. Using variations in the IAD deposition parameters, it is

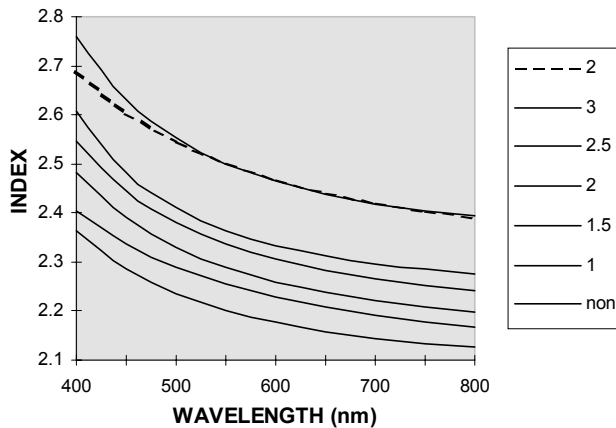


Figure 5. Refractive index comparison for films prepared as shown in Table I.

possible to deposit films with a refractive index at 560 nm up to about 2.55 or higher without any appreciable absorption in the visible spectral range. Data for the higher index films has been reported elsewhere (6).

If the moisture shift data is plotted as a function of the average ion current density exposure (see figure 5), then it can be seen that the level required to produce a moisture stable film is ~150 μA/cm².

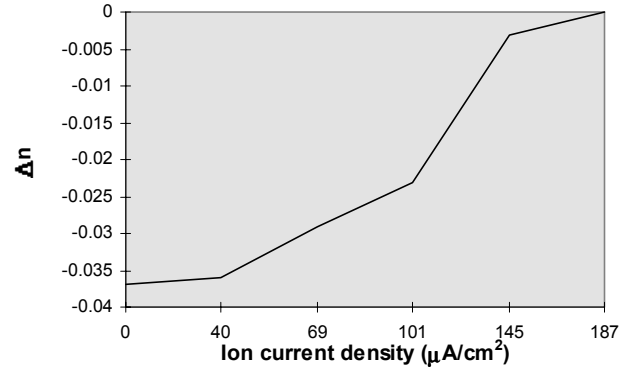


Figure 6. Moisture stability vs. Ion Current Density exposure for TiO₂ films.

Ta₂O₅ FILM DATA In a similar manner, Ta₂O₅ (tantala) films were deposited using various drive currents as a variable while maintaining all other deposition parameters. The films were prepared at 120°C substrate temperature and 6 Å/sec with chamber pressures of approximately 2x10⁻⁴ Torr for drive currents ranging from 1 ampere to 3 ampere in 0.5 ampere increments. The data for the films is reported in Table II. All of the terms are as defined previously for Table I. A non-IAD film prepared by the preceding parameters was so absorbing that it was not possible to obtain reasonable optical parameters. However, fairly good data (still somewhat absorbing) was obtained from samples deposited at higher pressures (3.5x10⁻⁴ Torr) and a lower deposition rate (3 Å/sec).

Table II.

#	D _I	CD _{avg}	n ₅₆₀	k ₅₆₀	Δn _{3λ/4}
non	0	0	2.041	~10 ⁻³	-0.044
95	1	41	2.168	0.0003	-0.015
81	2	90	2.129	<10 ⁻⁴	-0.005
92	2	90	2.178	~10 ⁻⁴	-0.009
86	2.5	118	2.119	0	-0.013
78	3	148	2.179	0	0

The current density profiles for the Ta₂O₅ films are the same as shown in figure 3 since the pressures required to make these films was the same as was used in taking that data (2x10⁻⁴ Torr). Unlike the TiO₂ films, the Ta₂O₅ films did not have as clear a relationship between refractive index, moisture stability and ion current density. A plot of the moisture stability vs. the O₂ ion current density is shown in figure 7. The Δn of -0.007 shown for the film prepared while being exposed to 90 μA/cm² ion current is the

average of the values obtained for runs 81 and 92. The data for run # 86 seems to be out of sync with the rest of the data. This shows up again when the refractive index data is compared.

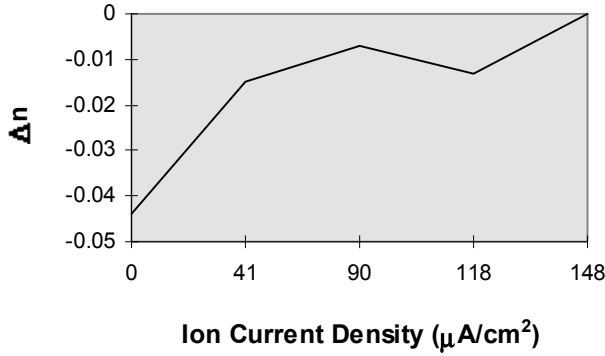


Figure 7. Moisture stability vs. Ion Current Density exposure for Ta₂O₅ films.

The index profiles for the Ta₂O₅ films are shown in figure 8. As indicated before, additional control of the refractive index is afforded by varying the pressure and/or deposition rate. Thus a film made using a drive current of 2 amps but a deposition rate of 4.8 Å/sec and another film deposited using 2.5 amp drive current and with a lower O₂ flow rate (resulting in a pressure of 1.6x10⁻⁴ Torr) produces a higher refractive indexes as shown by the dashed lines. However, although having a higher refractive indexes and improved moisture stability, neither film was completely moisture stable.

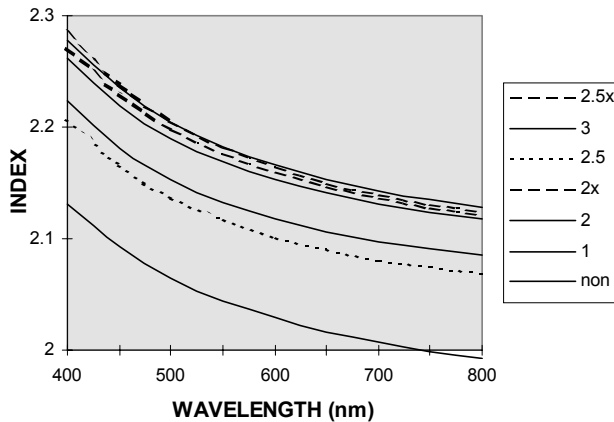


Figure 8. Refractive index comparison for Ta₂O₅ films prepared as shown in Table II.

Basically, an average O₂ ion current density of 145 μA/cm² seemed to produce moisture stable films of both materials. Since the traditional control aspects of deposition rate and pressure still apply, it is certainly possible that a lesser ion current density threshold might work for the stacks. The above work was done using a newer compact broad beam cold cathode ion source.

Previous unpublished work (7) in our facilities using a physically larger broad beam cold cathode ion source had resulted in moisture stable film stacks [Design (HL)⁶ where H and L are quarter wave layers of high and low index materials respectively] of titania, tantalum and niobia (Nb₂O₅) with silica (SiO₂) using conditions where the single layer high index films had a moisture stability (refractive index change) Δn of = -0.003. Unfortunately the setup used to produce these stacks was not as well documented as our later work (reported in this paper) so it is not possible to absolutely duplicate the setups and determine the ion current densities used for these stacks. However, we are comfortable in assuming that the ion current densities had to be comparable. Never-the-less we also know that the operational parameters within the plasma chamber of the ion source were different and that the ion energies may have been different.

Some of the data obtained from the stacks is reported in Table III. The ion source used had the capability of being used with various size apertures so this is shown as a parameter in the setup since stacks were made with two different size apertures. Spectral scans were made of the stacks in both a wet and dry with the results shown in figure 9. Measurements taken from the spectral scans showed bandwidths and T minimum at the center of the rejection bands as also shown in Table III. The index ratio (n_H/n_L) were calculated from the minimum transmission values using the relationship:

$$\frac{n_H}{n_L} = \left[n_s \frac{1 + \sqrt{1 - T_{\min}}}{1 - \sqrt{1 - T_{\min}}} \right]^{1/2} \quad (6)$$

These values are also shown in Table III.

These stacks are centered at various wavelengths since nothing was done to trim them in to specific values. The data in the tables show that there was an insignificant change in the H/L index ratios and the BW of the stacks for the wet and dry films.

TABLE III.
Data for 6 Period 12 Layer Stacks (HL)⁶

MTL(*)	Temp. (°C)	BW(%) HPW/ λ_0	n_H/n_L	
			wet	dry.
Ta ₂ O ₅ (non)	120	28.39-29.42	1.3554	1.3367
Ta ₂ O ₅ (40) x	120	32.51	1.4863	1.4867
TiO ₂ (non)	40	31.26-31.86	1.4537	1.4413
TiO ₂ (40) x	40	37.5	1.6410	1.6410
TiO ₂ (25)	40	37.18	1.6450	1.6437
Nb ₂ O ₅ (25) x	40	35.29	1.5498	1.5519

* non - no IAD, (##) - Aperture size for IAD - an "x" indicates data for stack with SiO₂ shown in plot in figure 9.

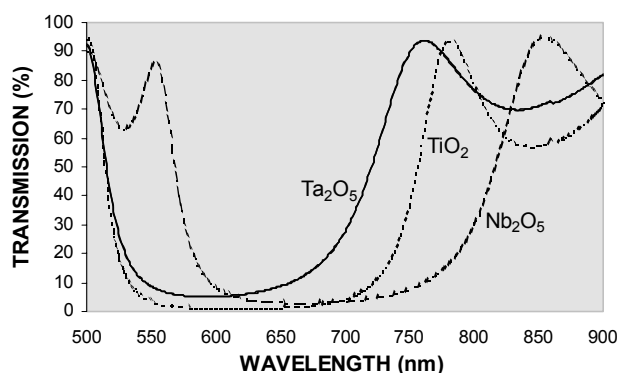


Figure 9. Spectral scans of moisture stable stacks (HL)⁶ where H is QWOT of high index materials indicated on the chart and L is SiO₂.

SUMMARY We have shown that high density moisture stable optical film stacks of TiO₂/SiO₂, Ta₂O₅/SiO₂, Nb₂O₅/SiO₂ can be produced if the films are exposed to an average O₂ ion current density of ~ 150 $\mu\text{A}/\text{cm}^2$ during deposition and using other parameters (temperatures, deposition rate and gas flow as reported here-in). Furthermore, we have demonstrated that lower ion current densities can also produce moisture stable stacks using lower pressures or lower deposition rates. It is also possible to make moisture stable stacks at higher pressures or higher deposition rates at higher ion current densities.

1) W. Essinger (1992) *Ion sources for ion beam assisted thin-film deposition* Rev. Sci. Instrum. **(63)** 11-5217.

2) James T. McNally (1986) Report No. AFIT/CI/NR 86-77D (Dissertation at Univ. of New Mexico).

3) John R. McNeil, Alan C. Barron, S. R. Wilson and W. C. Herrmann Jr. (1984) *Ion-assisted deposition of optical films: low energy vs high energy bombardment* Applied Optics **(23)** 4-552.

4) John R. MaNeil, G. A. Al-Jumaily, K. C. Jungling and A. C. Barron (1985) *Applied Optics Properties of TiO₂ and SiO₂ thin films deposited using ion assisted deposition* Applied Optics **(24)** 4-486.

5) H. A. Macleod *Thin Film Optical Filters*, 2nd edition, Macmillan Publishing Co., New York (1986) pp. 370-373.

6) To be presented at the Optical Interference Coatings Topical Meeting April 7-12, 1998 - Tucson Arizona.

7) Internal Technical Report DVI970002. Denton Vacuum, LLC. Moorestown, NJ.