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Plasmion Corporation

SBIR Phase II Project: Final Report

Project Title: Ultra-Smooth As-Deposited Optical Films

Contract Number: DASG60-02-C-0034

Period of performance: March 18, 2002 – March 31, 2004

Principal Investigator: Dr. Namwoong Paik, Plasmion Corp.

1. Identification and Significance of the Innovation

In the Phase I program, PLASMION demonstrated the capability of Negative Sputter Ion Deposition to deposit optical thin films with state-of-the-art properties, specifically ultrasmooth surfaces, high packing density, refractive index close to bulk values, and stability to environmental exposure. The objective of this Phase II program was to utilize these films to fabricate high-quality, economical optical devices for high energy laser applications. Prototype dielectric mirrors will be delivered which have higher reflectivity, lower loss, and higher laser damage threshold than currently available technology, with lower projected costs per unit.

PLASMION accomplished these goals by designing and constructing a flexible system for the fabrication of state-of-the-art thin film optical devices using Negative Sputter Ion Deposition. This system was used to fabricate the deliverable devices for the Phase II program, and will also serve as the platform for PLASMION's planned commercialization of optical thin film deposition equipment in Phase III.

Dielectric mirrors were fabricated using tantalum oxide and silicon oxide, two of the optical thin film materials demonstrated in Phase I. The target application is a high reflectance mirror at the YAG wavelength (1.06 microns) with high laser damage threshold. This final report details the development leading to this goal.

With this Phase II program, PLASMION has provided the groundwork to supply the Army with high reflectance mirrors and other devices for high energy laser applications which have better performance and lower projected cost than any currently available. The development will also provide tremendous commercial benefit by providing a breakthrough in optical thin film deposition equipment with application to a wide range of emerging markets in communications and next-generation lithography.

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1.1 Introduction

Optical Thin Films

Thin films are widely used for optical applications; these may be roughly divided into low and high technology categories. Low technology coatings (a relative term) includes single coating antireflection coatings and mirrors, as well as wear- and scratch-resistant coatings for lenses, windows, and other elements. A main concern with such coatings is cost and simplicity. Ion beam and other advanced coating techniques, although used in many such applications, are not strong candidates for improvements in low technology coatings because they will almost always have higher cost than non-vacuum methods such as dip-coating.

High technology coatings are those which require multiple coatings and which have exacting tolerances for important materials properties. Examples of these applications are optics for high energy lasers and filters for dense wavelength division multiplexing (DWDM). In the first case, due to the very high energies involved, optical elements such as mirrors must have almost perfect reflectance with the lowest possible losses; even a loss under 1% from absorption could result in extreme heat buildup and catastrophic failure. In the case of DWDM filters, extreme precision is required in refractive index, thickness, and uniformity, in order to resolve extremely closely spaced communications channels. For high energy laser mirrors, the difficulty in preparing materials of sufficient quality has resulted in very high costs for optical elements, inhibiting the ability of high energy laser technology to penetrate the commercial marketplace. For DWDM filters, the difficulty in preparing reproducible, stable thin films results in extremely low yields of usable devices (less than 1% yield is a common occurrence). Thus both of these technologies require breakthroughs in thin film deposition to achieve current and future goals.

Many in the optical device industry believe that ion beam deposition is the best hope to improve film quality for demanding high technology applications. The technical reasons for this potential are:

High film density. Conventional film deposition invariably produces films with a columnar growth mode, with interstitial cracks between columns penetrating the entire thickness of the film. This means not only that the films are less dense than theory (thus have lower refractive index), but also that they will be susceptible to moisture uptake on exposure to ambient. The effect of moisture is usually to change the refractive index and effective film thickness as a function of relative humidity. This environmental variability is especially damaging to DWDM filters as it can completely change their center wavelength with time. The extra energy transferred to depositing atoms in energetic growth methods tends to compact the film during growth a eliminate interstices and voids. Of the various energetic deposition methods available (laser assisted growth, ion assisted deposition, and others) ion beam deposition is the most effective in producing dense films.

Ultrasmooth films. The additional energy of the depositing atoms in ion beam deposition gives the atoms a high surface mobility after they strike the film. This results in an ability of the atoms to "seek their own level" on the growing surface and can yield films which have lower roughness than the original substrate. Surface roughness is important for optical scattering losses. Figure 1 shows the effect of surface roughness on scattering losses as a function of wavelength.

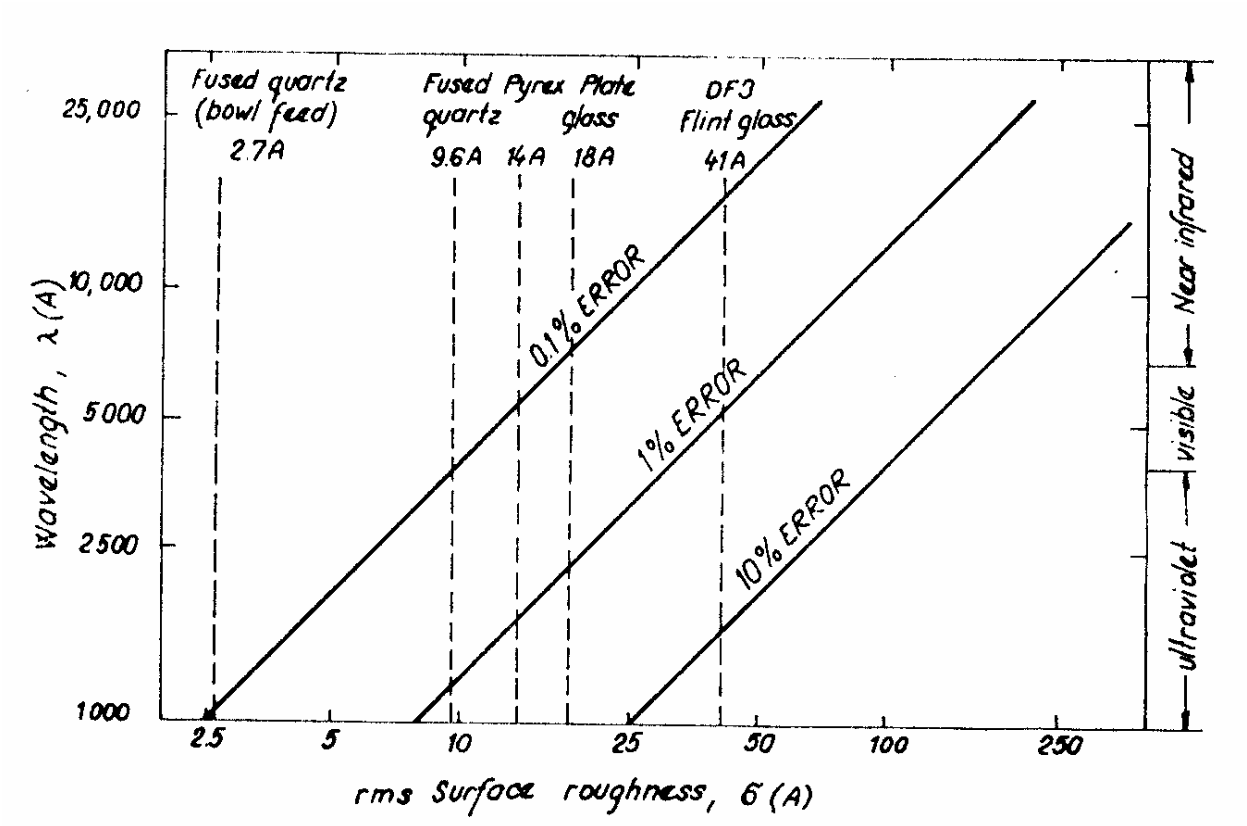

Figure 1. Effect of surface roughness on error (scattering loss) as a function of wavelength.

Sensitivity to flaws. Conventionally deposited films suffer a sensitivity to flaws caused by imperfections on the substrate surface and/or the presence of particulate contamination on the surface before deposition. Typically, any flaw in the substrate will propagate through the growing film and even become larger as film thickness increases, resulting in optical distortions and scattering losses. Studies have shown that ion beam deposited films will "heal out" such flaws as the film grows, rather than propagating them. This phenomenon occurs for the same basic reason as improvements in surface smoothness as discussed above: the increased mobility of depositing atoms tends to flatten and planarize the film.

Thus ion beam deposition is recognized as having great potential to solve pressing problems in high technology optical films. As will be discussed below, PLASMION's DMIBD has particularly great promise compared with other ion beam technologies.

PLASMION's DMIBD Technology

The use of low energy ion beams for growth, surface modification, and doping of thin films is an area of intense interest. The additional kinetic energy carried by the ions can be used for reactive ion etching or cleaning,[1] control over growth morphology,[2] nucleation control,[3] controlling epitaxial orientation,[4] and growth of metastable materials,[5] among others. Ion beam deposition has advantages over other "activated" growth methods, such as photo-enhanced and plasma-enhanced deposition, because the depositing species *themselves* rather than an auxiliary source possess the additional energy. This allows direct transfer of energy to the bonds formed with surface atoms. Dr. Ishikawa, Kyoto University, one of the pioneers in the field, uses the term "kinetic bonding" for the process.[6]

Ion beams for film deposition have been generated from gas plasmas,[7] cathodic arcs,[8,9] seeded beam supersonic free-jet (SSJ),[10] Colutron ion beam,[11] ion cluster beams (ICB),[12] ion beam sputtering,[13] and direct ion beam deposition.[14,15,16] Of these, direct ion beam deposition (DIBD) has particular advantages: low background gas pressure, so that the ion beam energies are not lost to collisions during deposition; freedom from particulates and neutrals; wide variety of possible ions which can be deposited; and a relatively narrow energy distribution without the need for filtering. The proposed project will employ PLASMION's form of direct ion beam deposition called negative metal ion deposition or NMIBD.

PLASMION technology utilizes a cesium ion source to bombard a solid target and create a negative metal ion beam. This results in an intense beam which can easily be controlled from 5 to 500 eV, a range that is particularly useful for materials synthesis, with a narrow energy distribution. The choice of metal ion which can be deposited is virtually unlimited. The advantages of PLASMION technology are described below.

<u>Direct Metal Ion Beam</u> – without a gas source, a major source of impurities such as hydrogen is eliminated, as are source limitations.

<u>Particle Free</u> – NO particulates are generated.

<u>Negative Ions</u> – all other ion beam technologies generate *positive* ions; *negative* ion beams have far less problems with charging of insulating or semiconducting substrates. Ion beam deposition always causes the ejection of secondary electrons from the substrate. When negative ions are deposited, they tend to balance the effect of the lost secondary electrons, reducing substrate charging, whereas positive ions tend to magnify the charging effect.

Scalability – Cathodic Arc Deposition and Laser Ablation are basically point source deposition techniques, and thus are difficult to scale up for industrial applications. PLASMION's process does not have these inherent limitations and is easily scalable for large area deposition.

Compatibility – PLASMION's large area source has a structure which is similar to magnetron sputtering, and thus is easily compatible with existing processing equipment.

These technological advantages translate to unique materials synthesis capabilities, unequaled by any other available technique. These include:

- Low Temperature Deposition. One can deposit high-quality materials on lower cost substrates – such as plastics or glass – and avoid problems with unwanted reactions or loss of volatile components common at higher substrate temperatures.

- Ability to Form Metastable Phases. DMIBD has been used to create films of synthetic amorphous diamond (a-D) and carbon nitride (C_3N_4).

- Control of Nucleation and Epitaxy**.** The extra energy of the deposited ions gives atoms additional mobility on the surface, which promotes the formation of large grains and epitaxial (oriented crystalline) layers at lower temperatures than conventional techniques.

- Atomically Smooth Surfaces. The energetic ion beams of DMIBD yield thin films with extremely smooth surfaces; in fact even smoother than the original substrate.

- Improved Adhesion, Reduced Strain. DMIBD can create a graded interface for superior adhesion and strain reduction.

- Conformal Coatings. Unlike other PVD processes which are strictly line-of-sight, PLASMION's NMIBD has demonstrated the ability to create uniform thin coatings over steps and in trenches. This ability also translates to an ability to heal flaws during film deposition.

The main competitive advantage of PLASMION technology can be summarized in the following way: it is the only efficient, well-controlled energetic deposition process that is suitable for industrial use. It has the capability to provide considerably better performance than currently available industrial processes at similar cost.

PLASMION technology outperforms biased sputtering for thin film production by a wide margin. Biased sputtering is inherently inefficient in delivering increased energy to the deposition process, because only a fraction of the deposited atoms are affected by ion bombardment. This results in films with relatively low density and smoothness. With PLASMION DMIBD, all atoms are energized during deposition; the efficient energy transfer produces harder, denser, smoother films with excellent adhesion.

At the same time, the structure of PLASMION's large area ion beam source is very similar to that of a standard magnetron sputtering head. This will make the technology easy to integrate into existing equipment, easy to scale up, and economical. This new ion source has just been developed in the past 18 months, and is the first large area direct ion source to be commercially available. A schematic of the PLASMION source and its operation are shown in Figure 2.

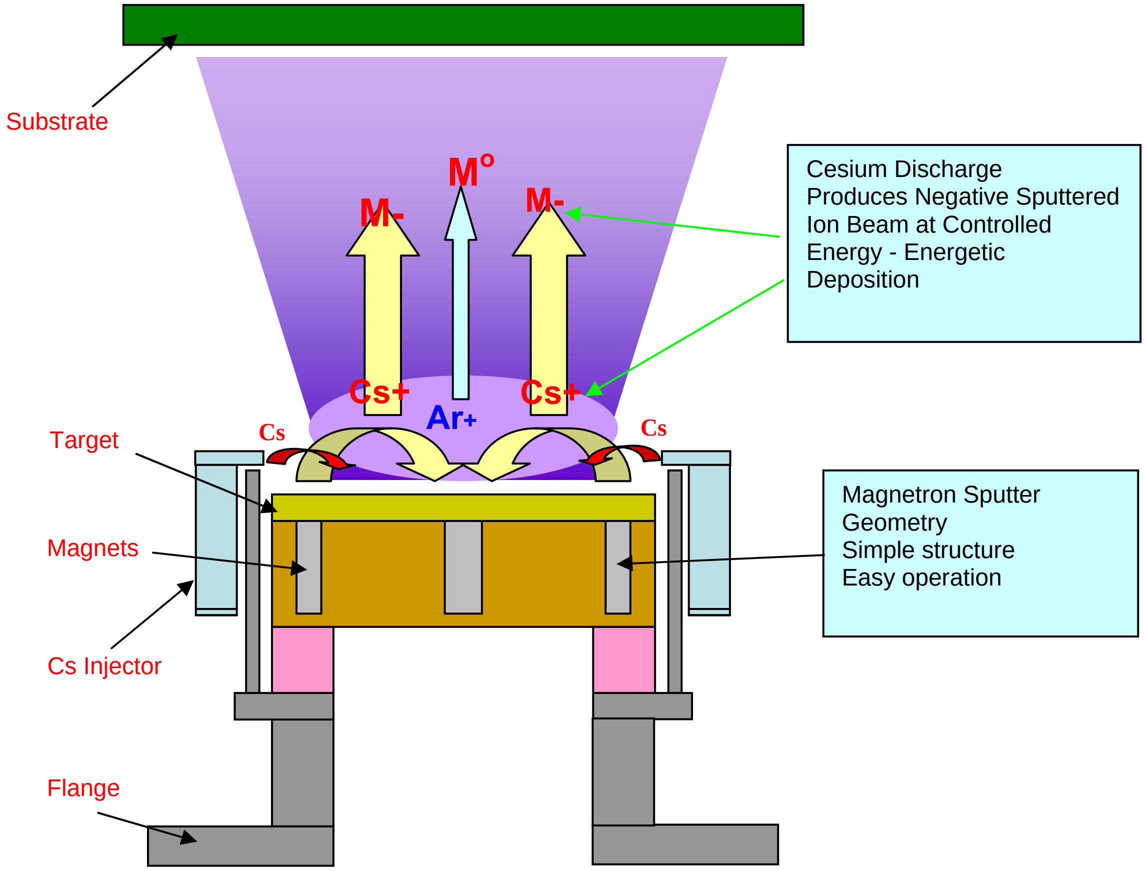

Figure 2. Schematic representation of PLASMION's large area ion source used in the project

A picture of the new source in operation is shown below in Figure 3.

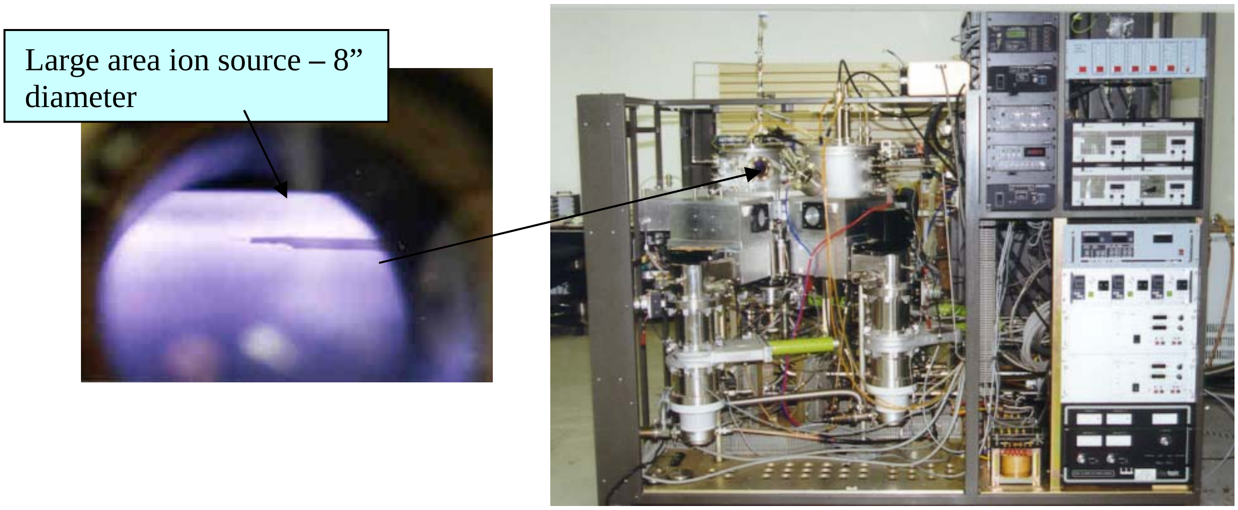

Figure 3. PLASMION’s 8” diameter ion beam source (inset) and four-chamber cluster deposition tool (right).

1.3 Phase II objectives

The goal of this project was to develop and deliver high reflectivity dielectric mirrors which have higher reflectivity, lower loss, and higher laser damage threshold than currently available technology, with lower projected costs per unit. In order to achieve this goal, we carried the Phase I results on individual optical films forward to focus on **material quality** and **process control**.

Material quality is essential for achieving low loss and high laser damage threshold. Loss is expected to come from two sources: absorption and scattering. Absorption loss is mainly a function of material purity and extent of oxidation. Scattering loss is affected by the presence of particulate impurities introduced during deposition, inhomogeneities due to porosity and material variations, surface and interface roughness, and crystal lattice defects. These factors were addressed in the first half of the program, as we investigated and optimized deposition conditions.

We recognized, however, that tradeoffs usually exist in optical materials properties: the factors that reduce absorption to the lowest levels generally do not simultaneously yield the lowest possible scattering, and vice versa. Thus we sought to understand what tradeoffs exist, and chose the conditions that achieved the best compromise of material quality for the specific high energy laser applications of interest to the Army. Laser damage threshold is the key property to be optimized, and this property is dependent on loss; however, depending on the pulse duration of the specific laser system used, different loss mechanisms dominate laser damage threshold. If the pulse duration is relatively long, total power is the important factor for damage, and absorption loss will be the dominant loss mechanism causing failure. On the other hand, if pulse durations are short, scattering will be more important to control, with absorption less of a factor. Based on our information about the lasers of most interest at White Sands, we expected that short pulse durations are most relevant and so focused on eliminating scattering in optimizing material properties. However, in order to have the broadest applicability to high energy laser applications we investigated the interrelationships of deposition parameters governing the absorption/scattering tradeoff.

Process Control is the key to achieving multilayer devices of the highest quality and at the highest yield. Uniformity and repeatability of deposition over area and over time will be of utmost importance in making the targeted devices and especially in making them at economical prices. The second half of the program was mainly concerned with understanding the factors influencing process control, refining and optimizing equipment design, and developing a process envelope for highest performance and yield.

The overall goal of the Phase II project was to fabricate and test high reflectivity dielectric mirrors for high energy laser applications, demonstrate their superiority to current state-of-the-art devices, and transition the new devices to commercial production. To achieve this goal, we had the following technical objectives:

Objective	Status
1. Establish the capability of utilizing PLASMION ion beam technology for multilayer optical devices.	Completed[*]
2. Construct a flexible system for multilayer deposition.	Completed
3. Establish deposition parameters	Completed
4. Prepare and characterize test samples	Completed
5. Fabricate high reflectivity dielectric mirrors	Completed
6. Characterize the optical and physical properties of the mirrors	Completed
7. Assess the laser damage threshold	Completed
8. Explore additional film materials and devices	Completed
9. Address scale-up and commercialization.	Completed

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[*] Originally, strategic alliances with two outside partners were contemplated as part of this task; however, subsequently these laboratories decided not to participate, so all objectives were accomplished at PLASMION.

2. Deposition system assembled

Chamber for Optical Multilayer Coatings

A Deposition Vacuum Chamber for optical coatings must have a number of elements in order to achieve a controllable process in high vacuum:

1. Stainless steel chamber equipped with wall cooling (or heating) capability
2. Basic vacuum $1x10^{-6}$ Torr or better.
3. Cryogenic vacuum pump.
4. Optical or crystal in-situ monitoring of thin film thickness
5. Accurate substrate heating control.
6. High speed substrate rotation capability.
7. Controllable deposition rate for each material.

In order to develop its Ion Beam Thin Film Deposition method, Plasmion needed to use at least the same quality vacuum chamber as the optical industry uses for production of optical thin film filters. Therefore such a chamber was purchased and customized for PLASMION's Ion Beam Deposition Process. The vacuum chamber was acquired from BARR Assoc. Inc., a well-known USA company, which produces all kinds of optical filters and mirrors using Ion Beam Assisted E-beam Evaporation and Magnetron Sputtering. The chamber was used for production of optical filters including 200GHz DWDM filters.

For the vacuum chamber we prepared a place in the laboratory with a 3 phase - 200 Amp. electrical line, water line and compressed air line. The vacuum chamber needed modification for the Negative Ion Beam Deposition Process. Requirements for the modification of chamber included:

- installation of two 8" magnetrons with cooling water and process gas lines,
- installation of power supply for magnetrons,
- manufacturing and installation of Cs sources with power supply (Cs converts conventional sputtering process to ion beam deposition process),
- manufacturing holders and manipulators for Cs sources.

Figure 4: Represents the vacuum chamber purchased and modified for Ion Beam Deposition of Optical Coatings

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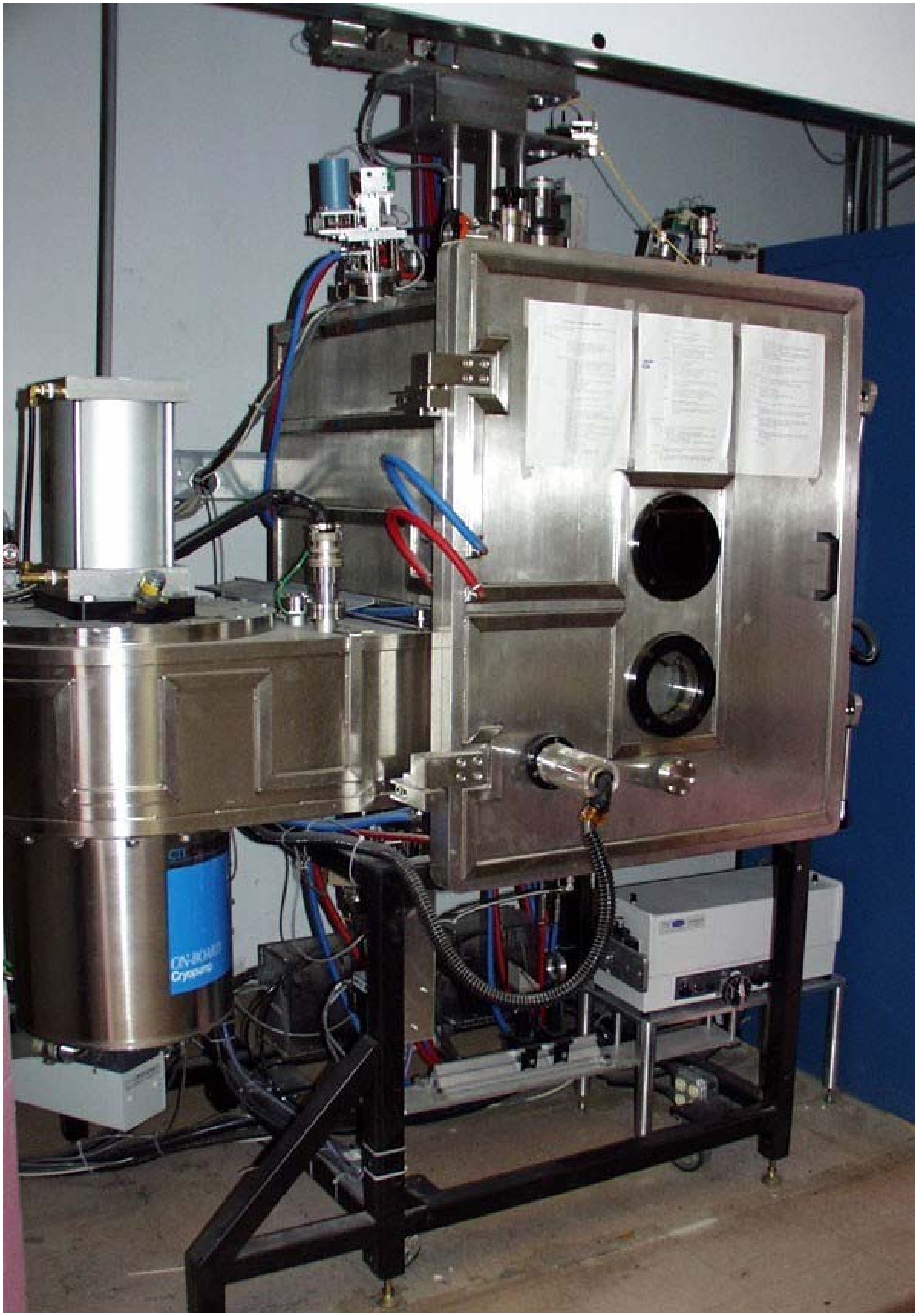
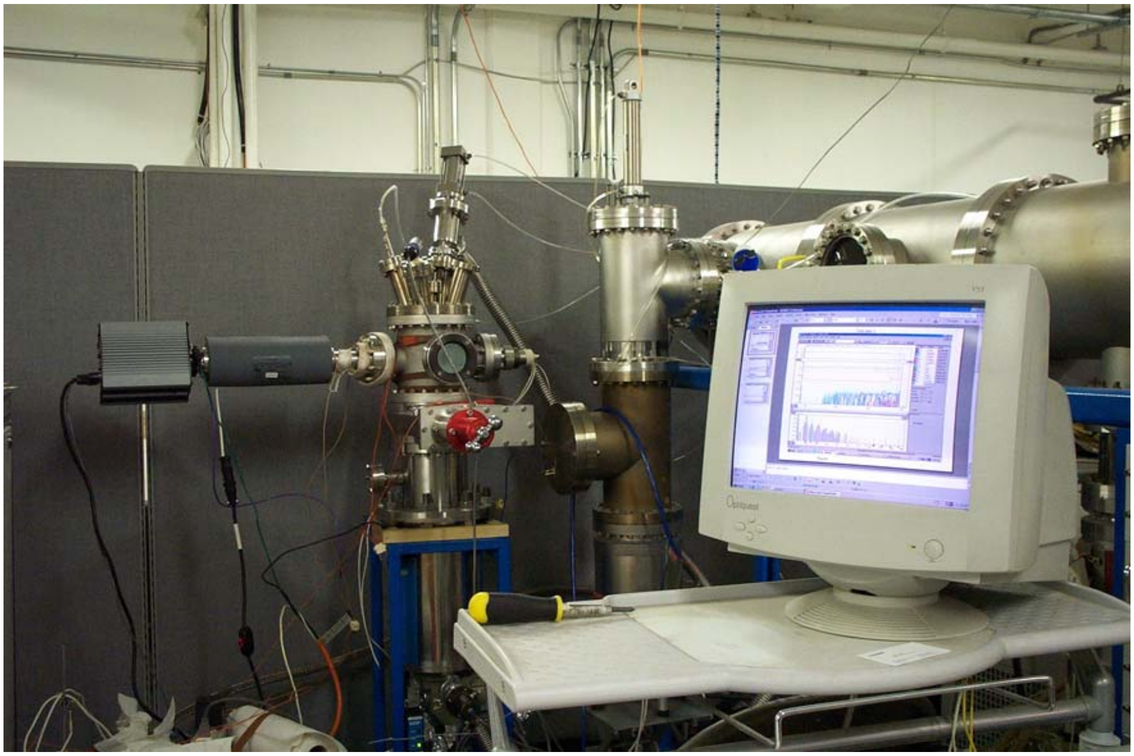


The Cs source is a very complicated device and is an important part of the vacuum chamber and process. Because the process is sensitive to the quantity of Cs on a surface of cathode of magnetron, during this project we tested different designs of Cs sources. These tests determined the Cs source design having the best reliability. For this purpose, Plasmion Corp. made a special vacuum chamber which consists of a Cs source and RGA – residual gas analyzer. In this chamber we were able to determine the flow of Cs, which is emitted from the Cs source in the presence of the process gases.

Figure 5: Represents the test chamber for Cs sources**.**



Based on experience with deposition of multilayer (10 – 150 layers) optical coatings by sputtering and e-beam evaporation, some requirements for an ideal Cs source can be formulated:

1. The Cs source must work in the environment of process gases, Ar/O2 50/50 %.
2. The Cs source must have a controllable flow of Cs, as required for each coating material (the necessary flow of Cs may depend on the type of coating material).
3. On/off time of Cs source must be less than 5 – 15 sec., the time for switching sputtering sources.
4. The Cs source must be stable for the same length of time for the coating flow of Cs within 10% accuracy.
5. The life time of the Cs source must exceed the time of the coating process - from 2 to 48 hours, depending on the design of the optical filter.
6. The Cs source must be able to be exposed to atmosphere during the exchanging of replacements parts.
7. The Cs source must have a reasonable price.

These requirements are very demanding, and at the start of this program a Cs source with such high parameters did not exist. As a first step, we used the original laboratory scale Cs source, which was not as flexible as an ideal source would be, i.e, it had a Cs flow varying over a wide range for 5-15 seconds. The second step was the design and development of a Cs source especially for the multilayer optical coating process.

The equipment for handling of Cs and all processes of making and testing cartridges were reviewed and improved where possible: leaks of Cs from cartridges were eliminated, cartridges with different quantity of Cs were made, the accuracy of temperature control of cartridges was increased and so on.

A lot of work was done on pellets. Pellets are parts of the Cs source, which are used to prevent the fast evaporation of Cs from the cartridges and to keep the flow of Cs constant. The pellets must have some optimum porosity. To find the optimum porosity, pellets with different porosity were made. The pellets were made from Cs_2O SiO_2 Al_2O_3 – a synthetic zeolite. The process of making this material was developed and patented by Plasmion Corp. previously and the process of pressing pellets was improved as well.

Fig.6 A photograph of the new glove box for handling Cs and loading it into cartridges in an Ar atmosphere.

Results of testing the Cs source

The main criteria for the Cs source is how it improves the properties of thin films; in particular, the surface roughness of the thin films. And secondarily, the lifetime of the Cs source is important. In other words if the Cs source makes the surface of films smooth, how long will this effect exist, especially in the presence of oxygen.

Depending on the process, the lifetime of Cs source must last from a few hours (one-two shifts for a box coating chamber, or small roll-to- roll machine) and up to a few days (for in-line coating machine, or roll-to-roll machine).

In our project we use the box chamber and deposition materials: SiO_2 and Ta_2O_5. The time of coating for the box chamber depends on the design of the filter or mirror and may be from 2 to 24 hours long. Deposition of SiO_2 and Ta_2O_5 requires the use of oxygen. When the filter is done the chamber must be open for the replacement of the substrate. While the chamber is open the Cs source is exposed to the atmosphere. Using the oxygen in a process and exposing the Cs source to atmosphere will cause the oxidation of Cs in a Cs source. In our project we have very difficult conditions for a Cs source.

But we can see another approach to delivery Cs in the deposition area. The best way to avoid difficulties with oxidation of Cs in the Cs source is to use not pure Cs in the Cs source but materials which contain Cs and don't oxidize in an oxygen atmosphere. These materials include: cesium iodide CsI, cesium nitrate $CsNO_3$, cesium silicate Cs_2SiO_3, cesium titanium oxide Cs_2TiO_3, and cesium tantalum oxide Cs_2TaO_3.

The method of delivery of material to the surface of the cathode may be evaporation or sputtering. By the nature of the process, the Cs mass deposition rate must be in a very low range. In terms of thickness equivalent, the deposition rate falls into the sub angstrom per second range. Because sputtering is a more controllable, more stable process than evaporation it is more desirable, but the Cs source will be more expensive. In the case of an evaporation type of Cs source, molecules of these materials under sputtering impact of ions from plasma will be divided into atoms on the surface of the target and in this way Cs will be liberated on the surface of the target. In the case of a sputtering type of Cs source, atoms of Cs will come onto the surface of the target.

After several months of experimentation in the test chamber, a Cs source was developed that satisfied all requirements for multilayer coating deposition. A diagram of the Cs source is shown in Figure 7 in exploded view. A photograph of an assembled Cs injector is shown in Figure 8. Figure 9 shows a drawing of the ring of Cs injectors assembled for mounting in the multilayer deposition chamber.

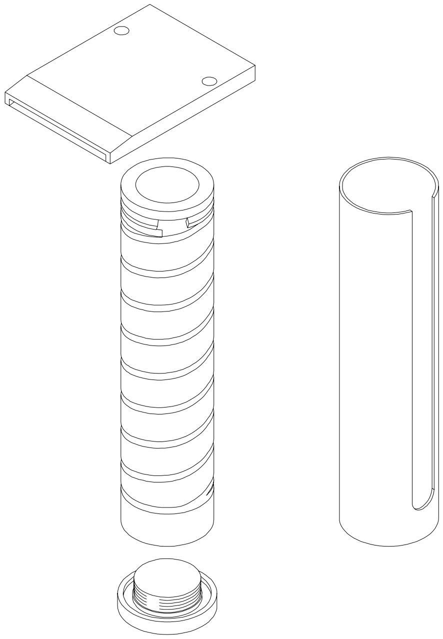


Figure 7. Exploded drawing of an individual Cs injector.

Figure 8. Photograph of an assembled Cs injector.

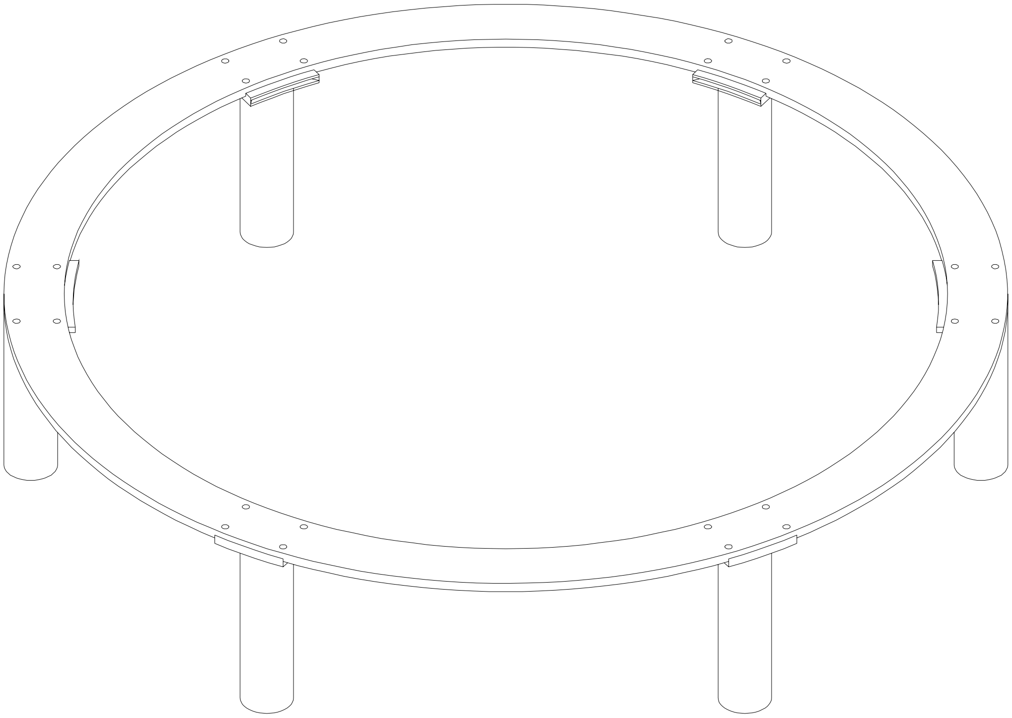


Figure 9. Drawing of ring structure holding Cs injectors.

Vacuum chamber for multilayer coatings

Because originally the Barr Assoc. vacuum chamber was designed and used for e-beam evaporation, we had to make some modifications and first of all to install magnetrons instead of e-guns. E-guns are usually located at the bottom of coatings chambers. Magnetrons have lower deposition rates than e-guns and must be closer to the sample spinner.

To find the right place for the magnetrons we performed calculations of uniformity of coatings as a function of the magnetron placement. The chamber has a spinning sample holder for optical parts of maximum size 8,5”. In order to achieve uniformity about .002 % it was necessary to install the magnetron guns on a radius 8.9” from the center of the spinner and at a distance 11” from the plane of the spinner. Adjustment of the heights of the magnetrons needed to be done after experimental evaluation of the uniformity of each material, because the plume of each material is different and each cathode is different (the magnetic field is different). Special holders, which gave us ability to precisely adjust the position of the magnetrons, were designed and made.

After these adjustments were made and optimized, the thickness uniformity shown in Figure 10 was achieved. The Cs injector ring was installed and tested in the chamber. At this point we were ready to deposit highest quality optical films.

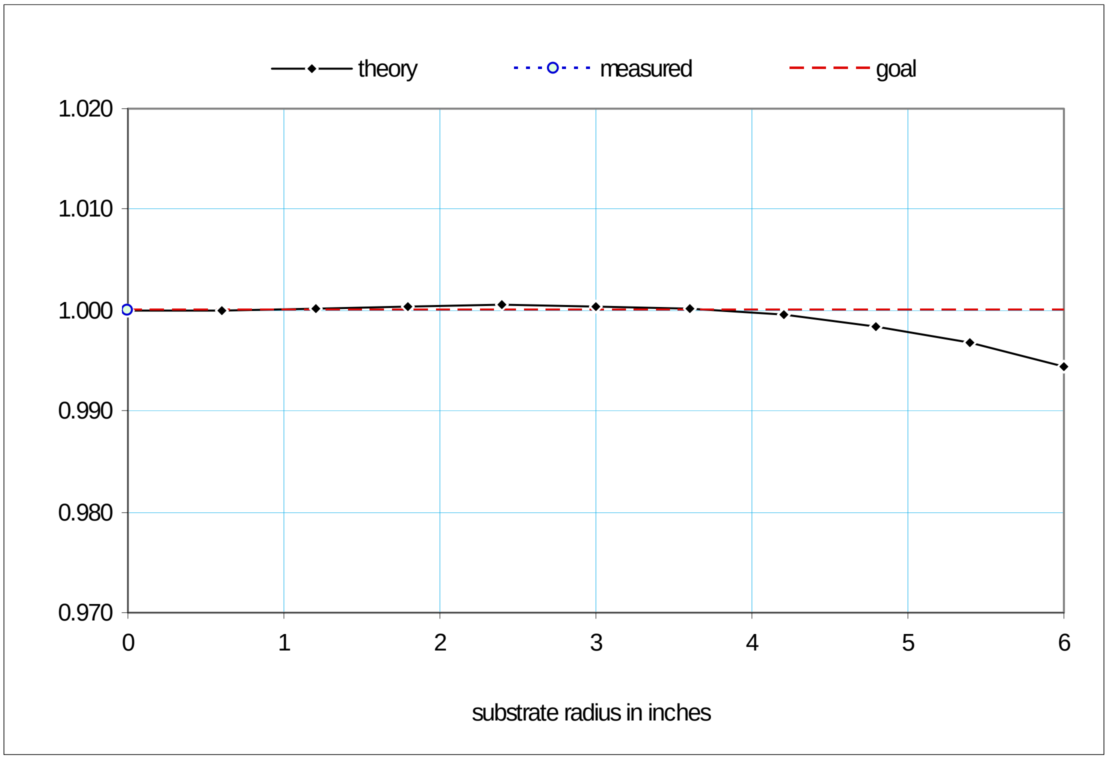


Fig.10 represents calculation of uniformity of coating

3. Experiment

3.1 Film Deposition

Initially, the deposition system was utilized to deposit single layer thin films of titanium oxide (TiO_2) and silicon oxide (SiO_2) on glass substrates. We worked with titanium oxide (TiO_2) -- one of the most extensively used coating materials with a high index of refraction, to investigate its suitability for the devices targeted by the program, compared to the usually employed tantalum oxide. It is transparent in the visible range and it has good mechanical properties as well as chemical stability. Among the several crystal structures (rutile, anatase and amorphous phase) of this oxide, rutile has the highest density and microhardness, the highest index of refraction and the highest temperature stability. For TiO_2 it is known that different types of deposition techniques create films with different properties. The best technique gives the highest index of refraction and the rutile crystal structure. Based on literature, we know that different sputtering and ion beam assisted evaporation methods produce TiO2 films with index of refraction 2.2-2.5 (for wavelength 550nm). We have gotten n=2.61 with extinction coefficient 8.3E-08 on a glass and silicon substrates by using Ion Beam Deposition Process. Index of refraction n=2.61 is approaching of bulk value with rutile structure. This result shows unique energetic properties of Ion Beam Deposition process.

The substrates used were 2 x 4” Corning glass. The substrates were cleaned before deposition by a standard aqueous alkaline cleaning, rinse in deionized water, acetone rinse and vapor degreasing in isopropanol. Furthermore the samples were precleaned before deposition by sputtering in argon for 1 – 2 minutes.

The deposition conditions were as follows:

Base pressure	10^{-6} Torr
Process pressure	1 – 3 mTorr
Oxygen partial pressure	1 – 3 x 10^{-5} Torr (balance Ar)
Sample rotation speed	200 rpm
Sputtering Power	1 – 1.5 kw

The target to substrate distance was approximately 8”. Deposition rates were 10 nm/min for SiO_2 and 5 nm/min for TiO_2. The thickness of the layers was monitored using a quartz crystal monitoring system, which was programmed for the correct densities and thicknesses of the films.

Examples of these single layer film samples are shown in Figure 11.

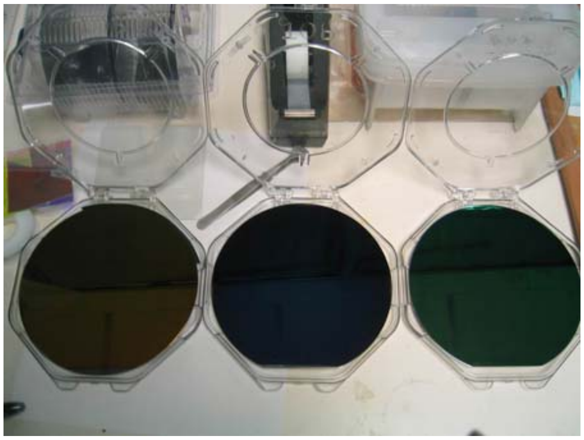


Figure 11. Photograph of silicon wafers with single oxide film layers. Uniform colors show uniform film thicknesses.

We ordered BARR Assoc. Inc. to prepare for us several samples of SiO_2 and Ta_2O_5 films by Ion Beam Assisted evaporation, in order to compare high quality films prepared via conventional methods to the project ion beam deposited films. The roughness of the BARR Assoc. films was tested by Atomic Force Microscope (AFM). We found that the films to be very smooth. The roughness of these films under investigation were comparable to SiO_2 and Ta_2O_5 films deposited by Plasmion's Direct Ion Beam method. Fig.12 and Fig.13 represent the roughness of SiO2 and Ta_2O_5 films deposited by Ion Beam Assisted Evaporation. Environmental tests showed no shift of transmission spectrum of SiO_2 and Ta_2O_5 films.

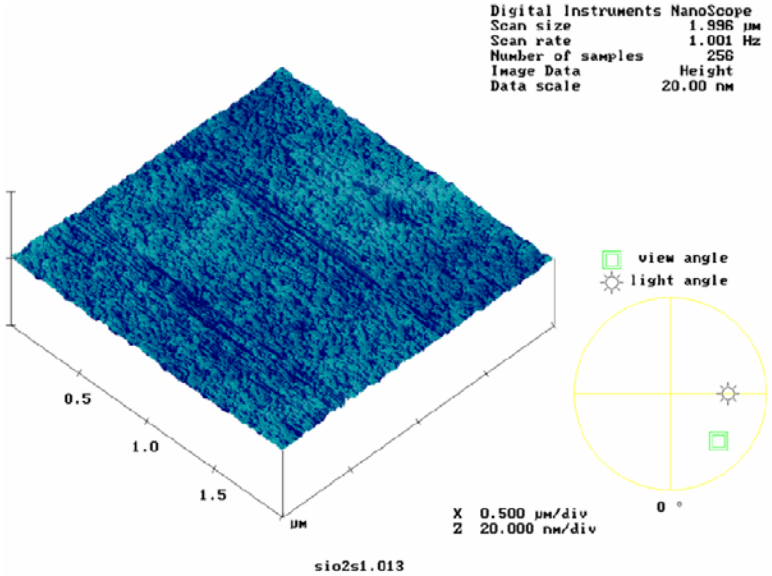


Figure 12. Perspective view of SiO_2 film deposited by Barr Assoc, by Ion Beam

Assisted Evaporation.

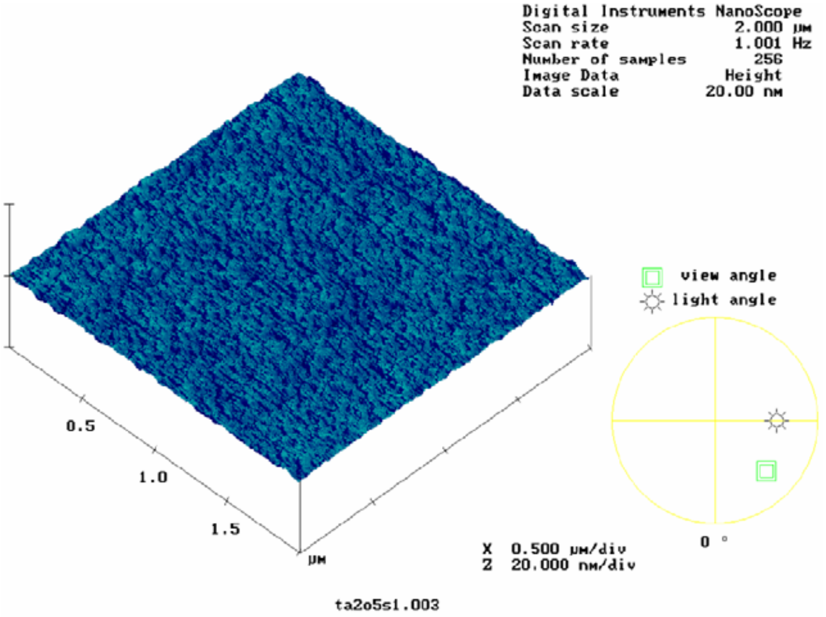


Figure 13. Perspective view of AFM scan of Barr Assoc. Ta_2O_5 film deposited by Ion Beam Assisted Evaporation.

These single layers SiO_2 and Ta_2O_5 films deposited by Ion Beam Assisted Evaporation have very good optical properties, low roughness and good environmental stability and so were used as a reference point for evaluation of properties of single layers deposited by Direct Ion Beam Deposition method.

Multilayer samples were then made in our chamber to reflect at wavelengths centered at 450 nm (sample #1, which had 8 total layers) and 570 nm (sample #2, which had 14 layers). Individual layers in the stacks had optical thicknesses (= physical thickness x refractive index) ¼ of the center wavelength. Films were uniform and specular. Photographs of these multilayer film samples are shown in Figure 14. The uniformity of color demonstrates the superior thickness uniformity of the deposition process.

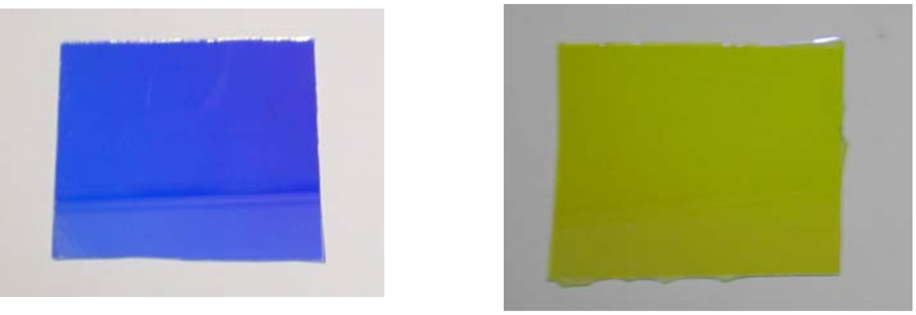


Figure 14. Photographs of multilayer film sample # 1 (left), which reflects at a wavelength centered on 450 nm, and sample # 2, at 570 nm. These samples were made on glass substrates.

Multilayer samples were also deposited with a design for the 1.06 micron center wavelength mirror as required for the project targeted device. Samples were prepared with and without Cs ion beam enhancement, in order to compare the properties of each type of film in laser damage threshold measurements. For these films, multilayer stacks of SiO_2 and Ta_2O_5 were used.

Additional Materials

Plasmion Corp. has produced different types of thin films with atomically smooth surface by negative ion beam deposition: Cu, C, ITO, SiO_2, TiO_2, Ta_2O_5. Among smooth surface thin films deposited by negative ion beam have high density, high environmental stability. For example we have achieved high density titanium oxide TiO_2 with index of refraction n=2.65 and k=0.000 for wavelength 550nm.TiO_2 with such a high index of refraction corresponds to rutile crystalline structure in the film. Other deposition techniques, like conventional sputtering and ion beam assisted methods, produce films with much lower index of refraction (n= 2.2-2.5).

The other example is ITO films. Conductive transparent thin films of indium tin oxide films are very desirable in organic light emitting diodes (OLED) display technology. Leading display industry companies at the present time use mechanical polishing of as-deposited ITO to get roughness less than 10A RMS. Plasmion's process produces ITO which doesn't need mechanical polishing.

3.2 Laser Damage Threshold Measurements

Laser damage threshold measurements were performed at Spica Laboratories. A schematic of their experimental setup is shown in Figure 15, with a photograph of the experiment in Figure 16.

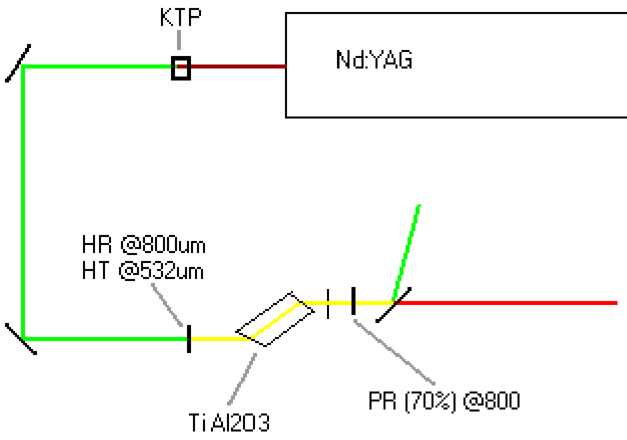


Figure 15. Schematic of LDT measurement setup used for project samples.

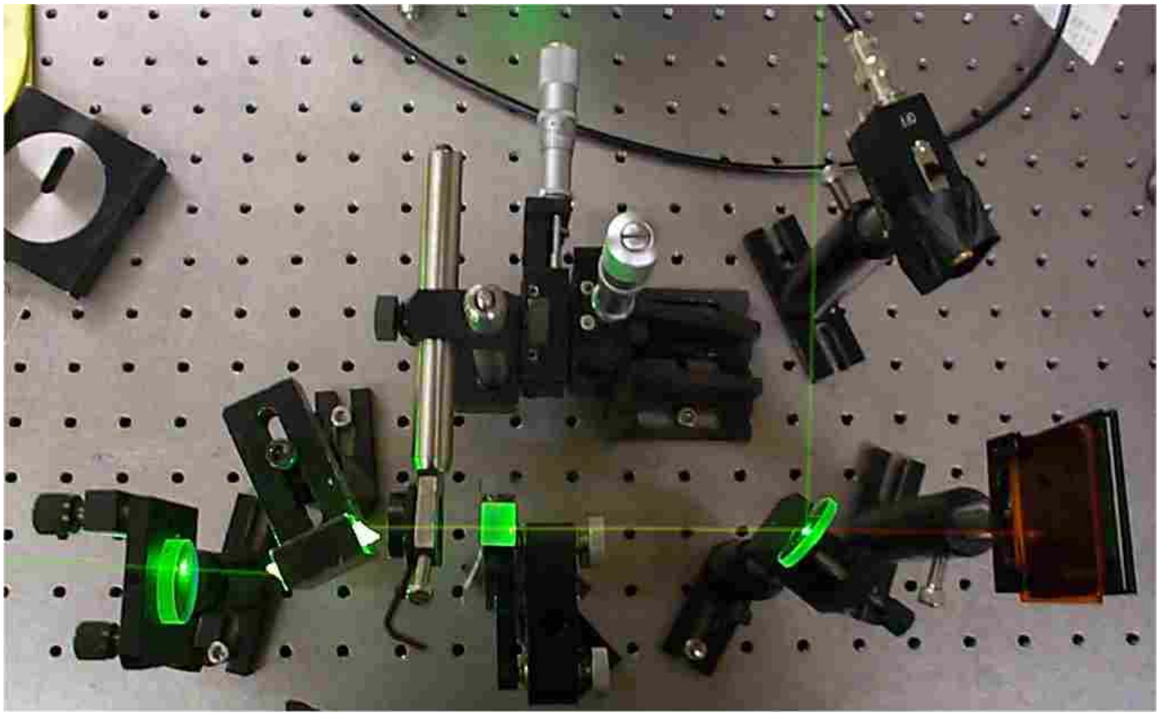


Figure 16. Photograph of LDT setup utilized for project films.

See the attached specifications sheet for the full conditions of laser damage threshold tests conducted by Spica Technologies.

4. Results Achieved

4.1 Optical Measurements

Optical measurements were carried out on the multilayer film samples shown in Figure 14. The measurements were performed on a Ocean Optics PC 1000 spectrometer in transmission mode. The spectrum of sample #1 is shown below in Figure 17, while #2 is shown in Figure 18.

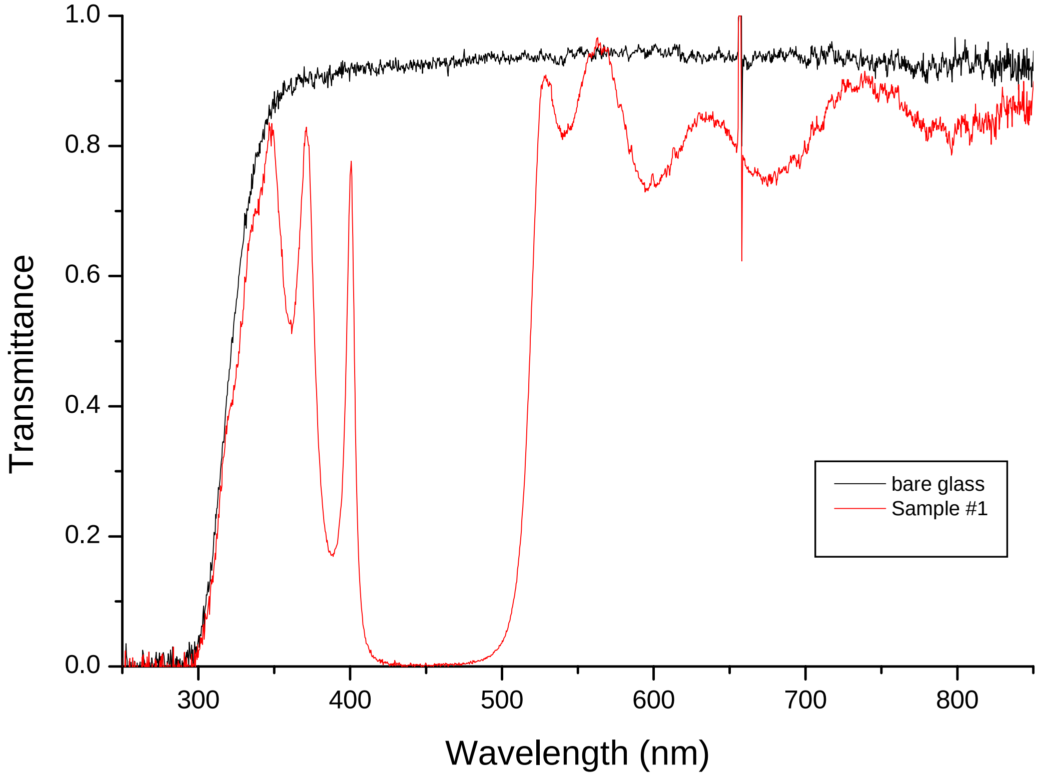


Figure 17. Transmission spectrum of multilayer sample #1, with center wavelength of 450 nm., along with spectrum of bare glass for comparison.

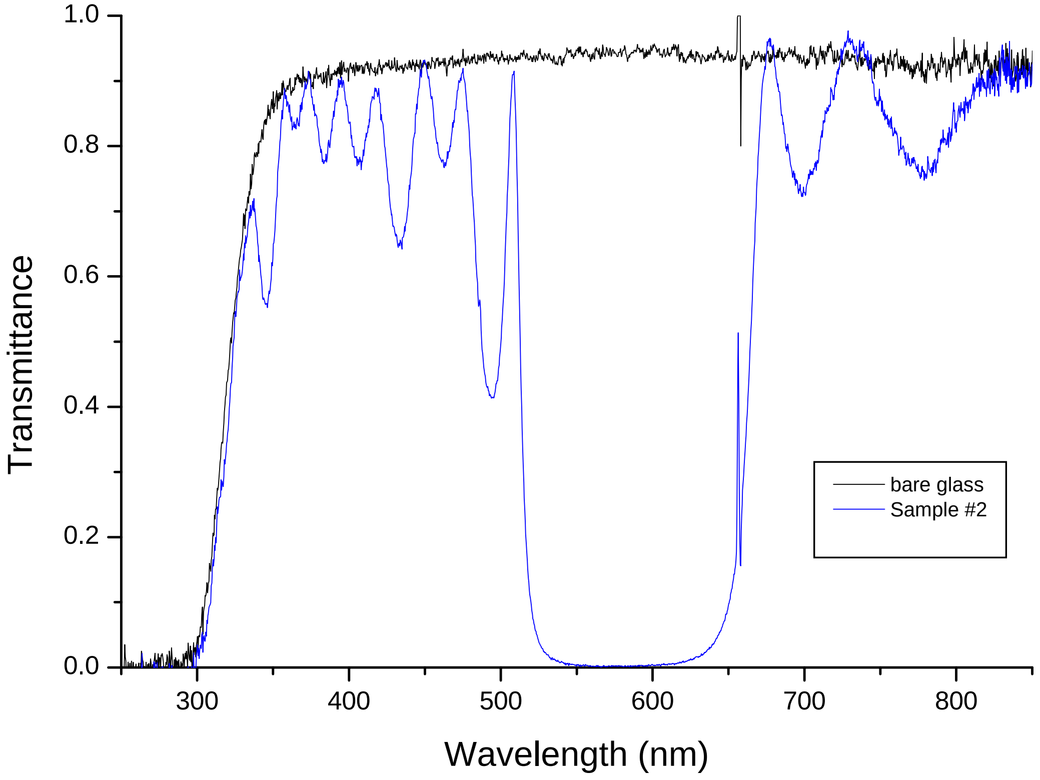


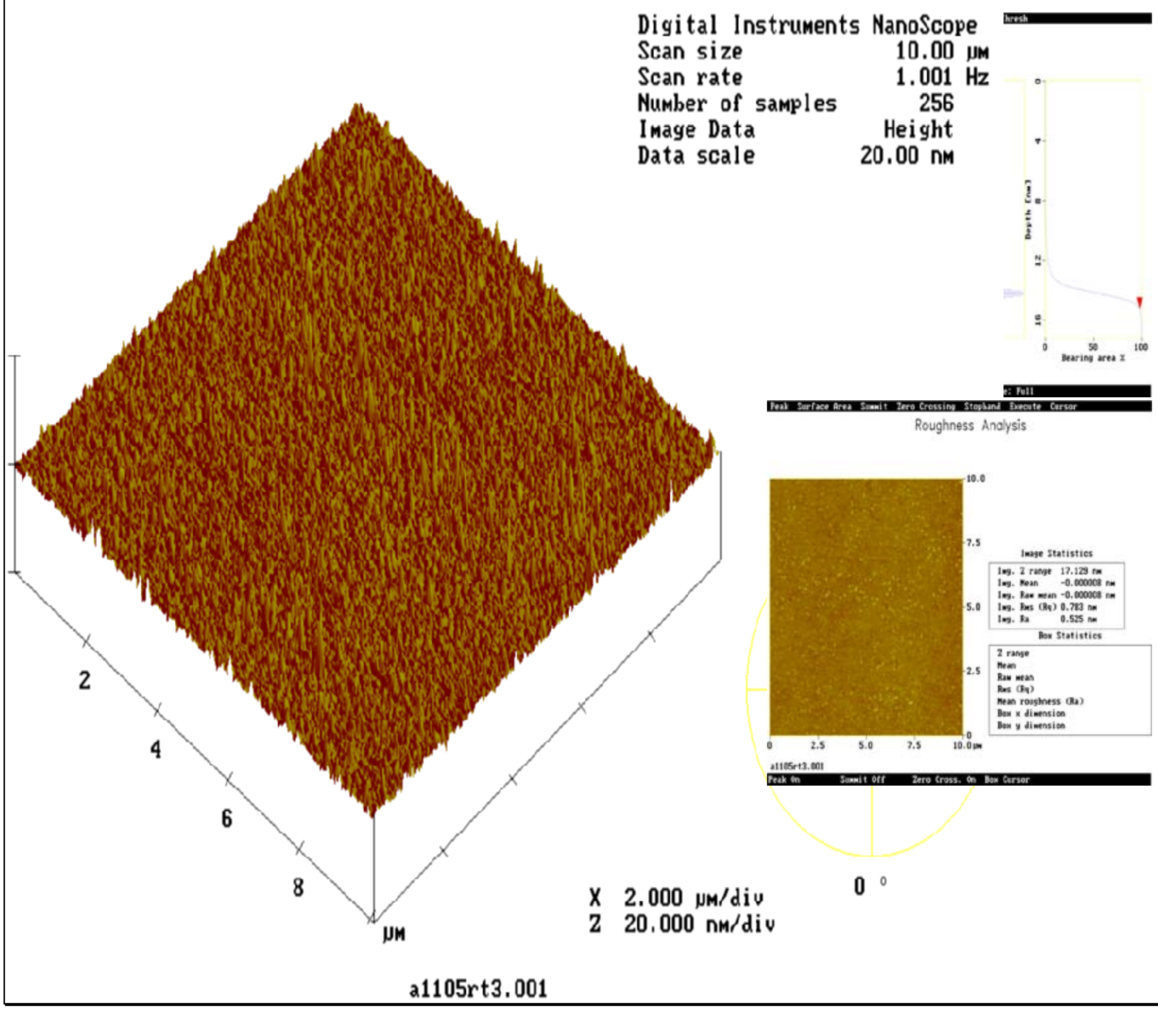
Figure 18. Transmission spectrum of multilayer sample #2, with center wavelength of 570 nm., along with spectrum for bare glass for comparison.

Note that both samples performed well, with essentially zero transmission for the calculated center wavelength in each case. The structure in the transmission data at other wavelengths is due to interference of the multiple films.

4.2 AFM Measurements

Roughness of the films was determined using atomic force microscopy (AFM). Typical surface roughness of Cs ion beam deposited films was less than one nm Ra. Figure 19 shows AFM data for an ITO/SiO_2 coating prepared as one of the alternative materials we investigated during the latter part of the program.

Thickness SiO_2/ITO; 5nm/150nm
Annealed 250 °C @ one hour
Rs 18 Ω/□ , peak to valley 3nm, RMS roughness <1nm



```
Digital Instruments NanoScope
Scan size               10.00 µm
Scan rate               1.001 Hz
Number of samples         256
Image Data             Height
Data scale            20.00 nm
```

```
Image Statistics
Img. Z range   17.129 nm
Img. Mean      -0.000008 nm
Img. Raw mean  -0.000008 nm
Img. Rms (Rq)  0.783 nm
Img. Ra        0.525 nm

Box Statistics
Z range
Mean
Raw mean
Rms (Rq)
Mean roughness (Ra)
Box x dimension
Box y dimension
```

Figure 19. Roughness measurement for ITO/SiO_2 film.

4.3 Laser Damage Threshold

The tables below show the results from the LDT measurements carried out by Spica for PLASMION films; measurements were carried out for films deposited both with and without Cs enhancement in order to assess the effectiveness of Cs ion beam deposition in preparing more laser damage resistant films.

Test Number	829	Fluence	Out Of	Damage	No Damage
Part Number	TF-111-829	0.078	10	0	10
Threshold	0.09	0.09	10	0	10
7-89		0.11	5	5	0
No Cs		0.143	3	3	0
P/Ag/S		0.4	3	3	0

Test Number	1291	Fluence	Out Of	Damage	No Damage
Part Number	TF-102-1291	3.45	10	0	10
Threshold	4.5	3.77	10	0	10
7-99/7-103		4.24	10	0	10
Cs		4.5	10	0	10
S/Ag		4.73	5	1	4

Test Number	1259	Fluence	Out Of	Damage	No Damage
Part Number	TF-101-1259	2.45	5	0	5
Threshold	3.43	3.43	10	0	10
7-102		3.8	5	2	3
Cs		4.15	5	3	2
P/S		5	1	1	0

Test Number	246	Fluence	Out Of	Damage	No Damage
Part Number	TF-104-246	1.88	5	0	5
Threshold	3.32	3.32	10	0	10
7-102		3.62	5	1	4
Cs		4.35	5	2	3

Test Number	273	Fluence	Out Of	Damage	No Damage
Part Number	TF-104-273	3.14	5	0	5
Threshold	3.8	3.56	10	0	10
7-102/103		3.8	10	0	10
Cs		4.08	10	4	6
Ag/P/S		5	1	1	0

Test Number	1275	Fluence	Out Of	Damage	No Damage
Part Number	TF-101-1275	2.27	5	0	5
Threshold	3.2	2.71	10	0	10
7-102/103		3.2	10	0	10
Cs		3.5	5	1	4
Ag/P/S		4.08	2	2	0

Test Number	860	Fluence	Out Of	Damage	No Damage
Part Number	TF-111-860	3.83	10	0	10
Threshold	4.42	4.17	5	0	5
7-104		4.42	10	0	10
Cs		4.72	5	4	1

Test Number	817	Fluence	Out Of	Damage	No Damage
Part Number	TF-111-817	0.15	10	0	10
Threshold	0.15	0.21	5	5	0
9994-1/7-39		0.62	2	2	0
No Cs		1	1	1	0
P/S		3.45	1	1	0

As can be seen in the tables, in all cases the Cs-prepared films outperformed the films deposited without Cs.

5. Targeted Device

In our Project thin films SiO2 (material with low index of refraction), Ta_2O_5 and TiO_2 (materials with high index of refraction) are important, because these materials have low absorption in UV-VIS-NIR of the spectrum region and are common for manufacturing of dielectric mirrors and filters. Ion beam deposition process may increase the threshold of laser damage because the smooth surface of thin films, less defects between layers and less scattering.

We designed a dielectric mirror with SiO_2 and Ta_2O_5 layers for a center wavelength of 1060nm. Calculations show that to get reflection more than 99.9% we need to use at least 21 layers, and a 27 layer design gives 99.99915% of reflection.

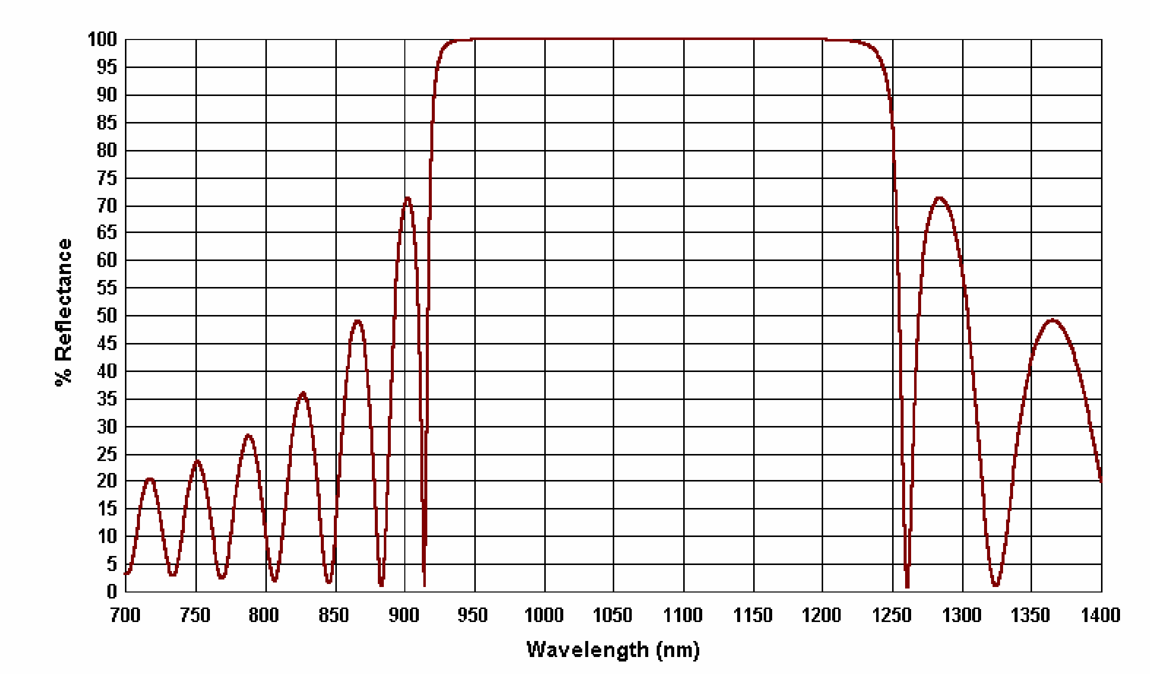
Results of calculation of a 27 layers mirror:

```
FilmStar DESIGN      FTG Software  Princeton, NJ       04-14-2003 15:47
------------------------------------------------------------------------
Design Wave 1060 nm        FWD ignore Side 2                Angle 0

                      Design (from substrate)
     1 .25H        2 .25L      3 .25H       4 .25L      5 .25H
     6 .25L        7 .25H      8 .25L       9 .25H     10 .25L
    11 .25H       12 .25L     13 .25H      14 .25L     15 .25H
    16 .25L       17 .25H     18 .25L      19 .25H     20 .25L
    21 .25H       22 .25L     23 .25H      24 .25L     25 .25H
    26 .25L       27 .25H

Film Indices                               Symbols: L,H:QWOT=.25
Indx    File
 Symb   $Funct    A(n)    B(k)     C      D      E      F      G
------------------------------------------------------------------------
  AIR          1.0      0        .      .      .      .      .
  SUB          1.52    0         .      .      .      .      .
------------------------------------------------------------------------
   L         1.46    0         .      .      .      .      .
   H          2.3     0        .      .      .      .      .
```

Reflection of 27 layers mirror (calculated):



6. Summary and Conclusions

In this program we set out to prove the utility of Cs ion deposited films for high power optical applications. This goal was fulfilled. Plasmion's process produced films of important dielectric materials with higher density and higher refractive index than films produced by any other deposition method. Further, laser damage threshold measurements proved that films produced with Cs ion bombardment were markedly superior to those produced by conventional techniques. Plasmion's Cs delivery technology was improved in several ways, including control, lifetime, reliability, and safety. A high throughput deposition system was built and tested. Single and multilayer films were produced for several operating wavelengths. A high reflectivity mirror operating at 1060 nm was produced as a deliverable of the program. The results of this Phase II program have shown Plasmion's NMIBD deposition technology capable of producing high energy optics with superior properties in an economical, scalable process. This result promises to enable new and superior optical devices for Army and commercial applications,

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