Coatings for Ultraviolet Lithography

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Abstract

Research into an optical thin film coating that enhances the current design of lithographic excimer laser gratings operating at 193 and 157 nm has been performed. The goal of such research is to improve durability and reflective efficiency. Possible coating materials include the fluorides, magnesium fluoride, barium fluoride, lanthanum fluoride and calcium fluoride. Each fluoride material was deposited on calcium fluoride and silicon substrates and tested for a variety of physical, optical and coating properties. The results from percent transmission tests and ellipsometric analysis were then used to characterize the materials and determine the index of refraction and extinction coefficients for the coating materials. Finally, a system calibration was developed in order to coat a final mirror with an enhanced aluminum reflector.

Background

The driving forces behind optical lithography improvements lie in shorter wavelengths of the light source and increasing numerical apertures of the projection lens. When such improvements are made, microprocessor features can be reduced in size by great orders of magnitude. Moore's Law, which predicts that semiconductor linewidth will halve every two to three years is currently in danger of becoming obsolete. Unless new technologies are developed which allow lasers to operate under extreme ultraviolet wavelengths, an alternative to optical lithography may soon become necessary. Currently, lasers operating under 193 nm are emerging from research labs and are beginning to operate within industry. 157 nm lasers are currently in development and pose an even greater challenge because of the millions of pulses of ultraviolet energy that each grating must endure $_{(3)}$. Such a high volume of pulses can cause failures in laser parts such as the gratings used in narrowing the spectrum to 193 or 157 nm. Gratings used in excimer lasers for lithographic purposes are exposed to millions of pulses in relatively short periods of time. The challenge is to build a grating that can withstand continuous pulses of high energy with a minimum of absorption.

Introduction

The challenge in creating an effective optical thin film coating lies in the fact that relatively few coating materials exist which can withstand the continuous bombardment of ultraviolet light that is required in lithographic applications. A layer of aluminum, protected by a layer of magnesium fluoride, currently coats the grating in excimer lasers. While the current grating is substantially effective as an ultraviolet reflector, a greater level of durability and reflectivity is desired. In order to increase grating durability and reflective efficiency, optical thin film coatings will be applied to the grating in alternating layers of materials of high and low refractive indices. Fluorides have been selected as possible materials to test because of their low absorption at 193 and 157 nm. An additional desirable quality lies in their low ultraviolet cut-off, which is at or below 140 nm $_{(1)}$. Fluorides also posses relative durability when exposed to continuous high-energy pulses. Disadvantages to using fluorides lie in their poor deposition properties. It is often advantageous to use heat or ion assistance to pack down the coating, thereby reducing porosity and increasing physical durability. Unfortunately, this process creates difficulties in coating gratings for industrial applications. As a result of this, the methods described above were not utilized. It should be noted that oxides were considered as a possible coating material because of their desirable refractive indices and better deposition properties, however, because of their high absorption at ultraviolet wavelengths, they were disregarded. After the final coatings are characterized, they will be deposited on a substrate in alternating quarterwave layers of high and low indices of refraction. A quarterwave is defined as the index of refraction, n of a coating, multiplied by its physical thickness, d, or

$$nd=\lambda/4$$

In order to determine n somewhat accurately, measurements of percent transmission are taken, and n and k are altered in order to assign a best-fit curve to the percent transmission data. Once n is determined, d, or the physical thickness can be determined according to the equation above. Characterization software calculates the physical thickness of the coating deposited. A simple proportion consisting of the thickness recorded by a crystal, or monitor in the coater, and the thickness calculated by the computer, can be used to calibrate the coater so that the desired thickness' are accurately deposited in the final coatings.

Coating Deposition

The BALZERS 19" coater was used to deposit coating materials onto substrates, utilizing the electron beam gun deposition method without the use of heat or ion assistance. During electron beam gun deposition, a hot filament emits electrons, which are formed into a beam by a magnetic field and directed onto the material to be evaporated. The coating material is held in a crucible that is water cooled, and the substrate is rotated above the crucible to ensure relatively even coating. The coater is vacuum pumped into the 10^{-5} to 10^{-6} Torr range using a diffusion pump before deposition begins. A crystal, which is located in the upper right hand corner of the coater, monitors the physical thickness of the coating. It is necessary in the final stages of design to make a calibration to adjust for the discrepancies between the position of the crystal and the position of the substrate in order to deposit accurate physical thicknesses.

Each coating material is initially deposited on a Crystalline Fused Quartz (CFQ) substrate, and coating properties such as deposition rate, electron beam emission current and sweep latitude/longitude frequency are noted. After physical tests are performed on the CFQ optics, 5000 angstroms of each coating is deposited on each of the following substrates: a 1" diameter single crystal Calcium Fluoride substrate, and a 2" diameter silicon wafer that is p-doped with boron, has an orientation of 1-0-0 and a resistivity of 1-10 ohms. The calcium fluoride coating material was deposited on 1" squares of UV grade fused silica. In an attempt to avoid crazing, 1000 angstroms of lanthanum fluoride were deposited instead of 5000. This will be taken into account during characterization but should have little effect on the final product because all layers of interest at 193 or 157 nm will be significantly thinner than 5000 angstroms.

The same scan is repeated and the results are compared to the baseline, creating a 100% reflectance line. In figure 1, the computer sets the value of R equal to 1. In figure 2, a coated optic takes the place of r_2, and r_2 is moved in front of the coated optic. The beam is reflected across r_1, r_s, r_2, r_s, and r_3 respectively, giving the equation

$$R' = R_o r_1 r_s r_2 r_s r_3$$

Since R is given to equal one, it can be substituted into the above equation giving

$$R' = r_s^2$$

The square root of r_s^2 is calculated by the computer, which represents the absolute percent reflection of the coated optic across the spectrum tested.

IV. Roughness

Roughness of a coated optic is measured in order to determine the surface structure of the coating. It is defined as any closely spaced irregularity in a surface such as cutting tool marks or irregular coating texture. Rayleigh's Law states that the intensity of scattered light (I_s) increases as wavelength decreases according to the equation

$$I_s = k\,\lambda^{-4}$$

where k is a constant and λ is equal to wavelength. Because of this property, it is necessary to minimize the roughness of a coating's surface structure in order to minimize the scattering of light. The roughness of the coated calcium fluoride substrates are measured using a WYKO surface profiler which scans the optic and calculates the root mean squared roughness over the entire measured array according to the equation

$$R_q = \sqrt{\frac{1}{n}\int_{i=1}^{n} (z_1 - \bar{z})^2}$$

where n equals the number of peaks across the measured array, and z equals the height of the peak.

Coating Properties and Test Results

Below is a summary of the results of the tests described above.

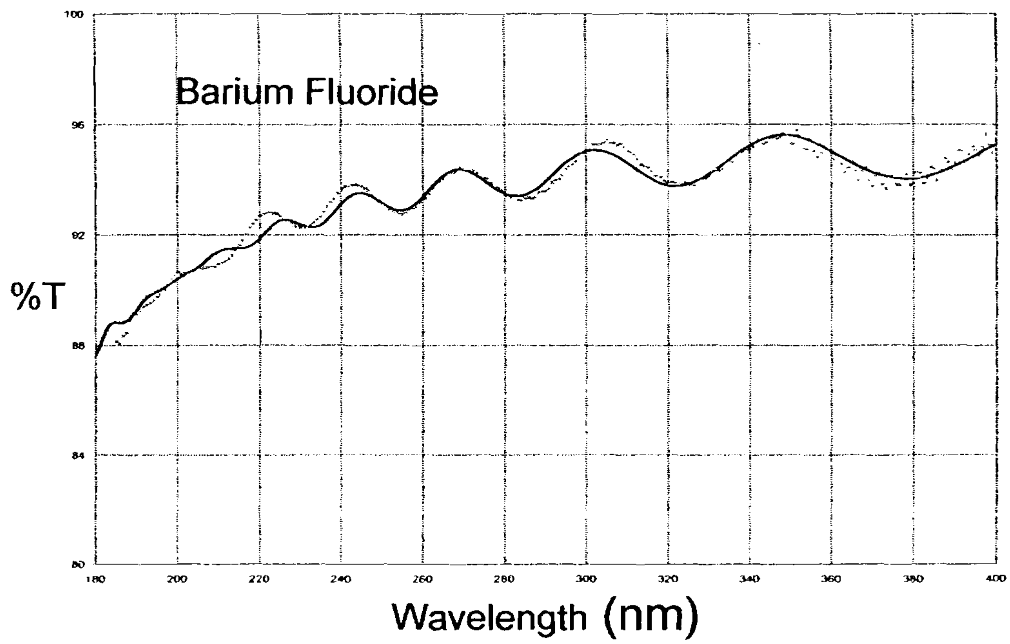
Coating	MgF_2	BaF_2	LaF_3	CaF_2
Substrate	CaF_2	CaF_2	CaF_2	fused silica
Tape Test (Pass/Fail)	P	F	F	F
Rub Test (Pass/Fail)	P	F	F	F
Root Mean Squared Roughness (nm)	42.95	65.55	71.85	71.48
% T Referenced to Substrate @193 nm	98.13%	97.08%	96.14%	95.27%
Absolute % Reflectance @193 nm	3.84%	5.16%	7.37%	4.25%
Emission Current (A)	0.02	0.02	0.02	0.02
Deposition Rate (Angstroms/sec)	3.0-5.0	0.5-1.0	1.0-2.0	8.0-10.0

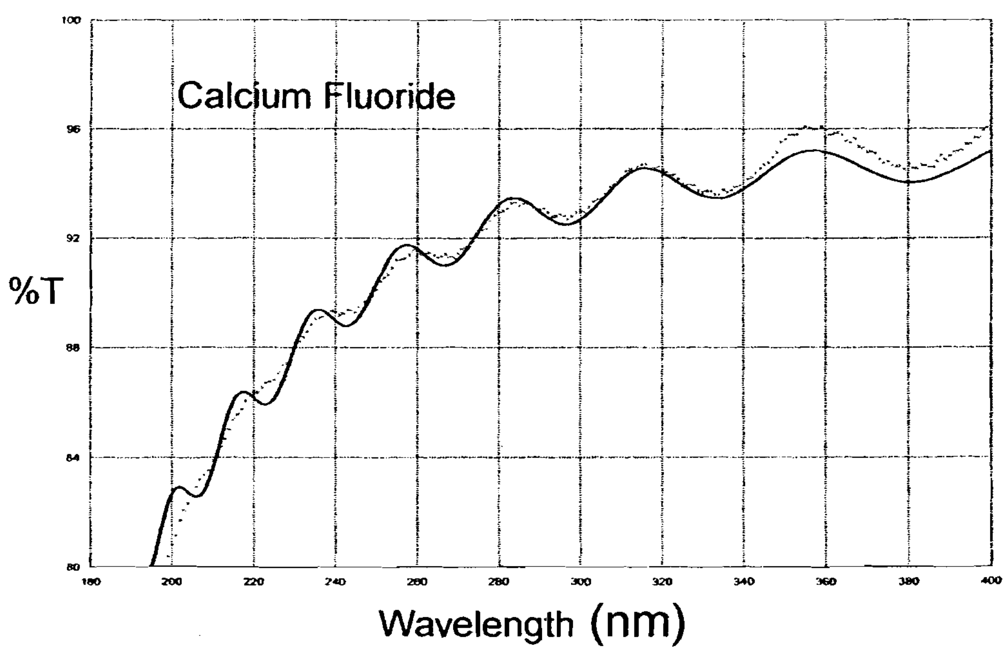
Characterization

I. Characterization and Design at LLE

The CARY percent transmission data is characterized using OptiChar for Windows Version 2.22 software. Characterization involves the altering of index of refraction values '*n*' and extinction coefficients '*k*', as a function of wavelength, in addition to the film thickness *d* and the inhomogeneity of *n*, to assign a best fit curve to the percent transmission data. Due to the crazing noted, lanthanum fluoride was disregarded as a possible high index material in the initial stages of characterization. Magnesium fluoride characterization yielded an index value that was too high when compared to reported values. Due to these factors, calcium fluoride was selected as the low index material, and barium fluoride was selected as the high index material.

Attempts to assign a best-fit curve are pictured below.





While these materials were chosen and used to coat a mirror, their selection is the result of the process of elimination. Characterization of barium fluoride yielded an *n* value of 1.6 compared to a reported value of 1.7 (4). Its *k* value was equal to zero compared to a reported value of 0.018 (4). Similarly, calcium fluoride yielded an *n* value of 1.13 compared to 1.39 (4). Its *k* value was calculated to be 0.0015 compared to 0.011 (4). Despite these discrepancies, a table of *n* and *k* values was produced as a function of wavelength. These values were used to calculate the physical thickness of the coating deposited on the samples. The physical thickness of barium fluoride deposited was calculated to be 7,170 angstroms while the physical thickness of calcium fluoride was calculated to be 11, 937 angstroms. Keeping in mind that the crystal monitor in the coater was programmed to deposit 5000 angstroms, we can set up a simple proportion for each coating material in order to deposit an accurate quarterwave layer. These proportions are listed below.

Barium Fluoride: 0.69735 = physical thickness recorded by monitor / actual physical thickness measured on substrate

Calcium Fluoride: 0.41887 = physical thickness recorded by monitor /actual physical thickness measured on substrate

OptiLayer software designed a coating by calculating the thickness of 1 quarterwave. Knowing the above proportions, the crystal monitor was programmed to coat a mirror with the following characteristics:

Barium Fluoride:	Physical Thickness = 362.544 Angstroms
Calcium Fluoride:	Physical Thickness = 532.683 Angstroms

Multiplying the optical thickness of each coating by its respective monitor to physical thickness ratio yields the physical thickness that must be deposited according to the coater monitor.

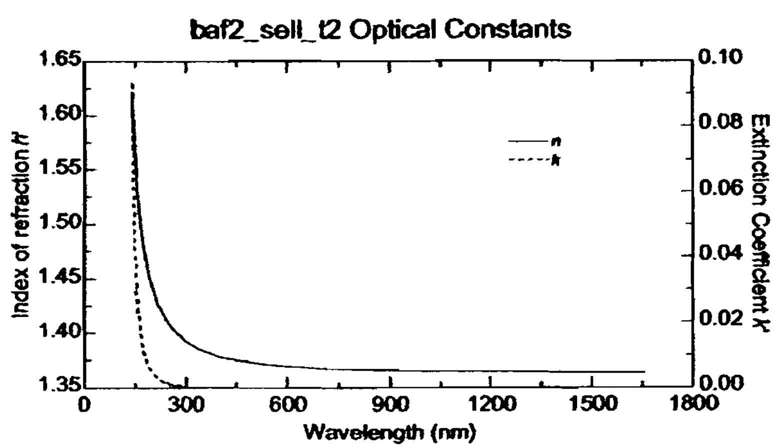
Barium Fluoride: Physical thickness deposited according to monitor = 253 Angstroms

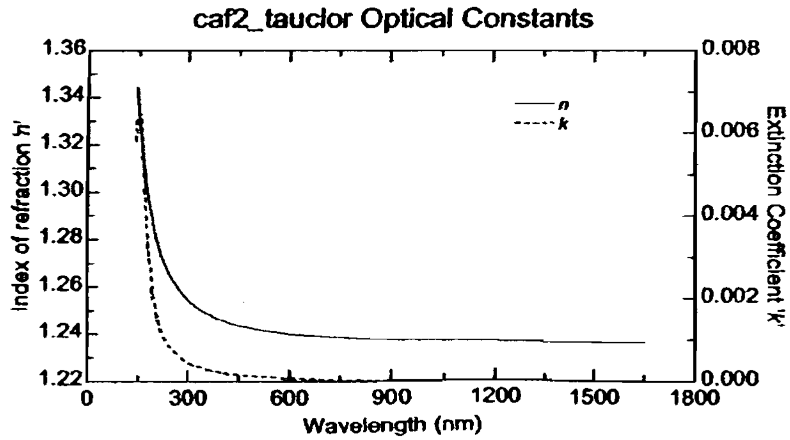
Calcium Fluoride: Physical thickness deposited according to monitor = 223 Angstroms

The final mirror was coated with alternating layers of barium fluoride and calcium fluoride, respectively. The results showed a significant increase in absolute percent reflectance, however, the peak of the coated aluminum curve occurs in the visible spectrum, not in the ultraviolet. In order to shift the peak, it is necessary to adjust the thickness' of the system by the multiplying by the percent desired peak divided by the current peak.

II. Characterization at J.A. Woolam Co., Inc.

In addition to being scanned on the CARY, the coated silicon wafer optics were sent to J. A. Woolam Company for Variable Angle Spectroscopic Ellipsometry (VASE) analysis in order to characterize film thickness and optical properties. Data was acquired over the spectral range of 146 nm to 1800 nm. Results from ellipsometric analysis are expected to yield more reliable results concerning film thickness and optical properties. *n* and *k* data is shown below (2).





Conclusion

Research into optical coatings for ultraviolet excimer laser gratings has been performed. Unfortunately, due to time constraints, this project was unable to be completed within the time allotted. My advisor will complete it by using the *n* and *k* data from elipsometric analysis performed by J. A. Woolam Company. Although the first mirror design yielded inaccurate results, one must keep in mind the difficulties encountered in both the deposition methods and spectrophotometer used. Due to the industrial implications of such a coating, it was recommended that each sample be made without heat or ion assistance, as it would be difficult to utilize such methods in the coating of an actual grating. As a result of this, the porosity of the sample coatings along with the CARY's inability to measure accurately in the deep ultraviolet spectrum contributed significantly to the final inaccurate results. On a more positive note, data regarding physical, optical and deposition properties for the fluorides was collected and will be utilized by the lab in the completion of this project and future endeavors.

I would especially like to thank my advisors Jim Oliver and Doug Smith for taking the time out of their busy days to familiarize me with both the labs and the theory behind my project. Thank you also to Mary Risely for collecting optical constant data and teaching me how to use the CARY. Especial thanks to Nelson LeBarron and everyone in OMAN for teaching me how to use the coater and always being there when it broke down. Finally, I would like to thank Dr. Craxton for selecting me to work at LLE and giving me the chance to experience scientific research.

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