The Optical Constants of Sputtered U and a-Si at 30.4 and 58.4 nm

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ABSTRACT

This paper is a report on our effort to use reflectance measurements of a set of amorphous silicon (a-Si) and uranium (U) multilayer mirrors with an uranium oxide overcoat to obtain the optical constants of a-Si and uranium. The optical constants of U, its oxides, and Si, whether crystalline or amorphous, at 30.4 and 58.4 nm in the extreme ultraviolet (EUV) are a source of uncertainty in the design of multilayer optics. Measured reflectances of multilayer mirror coatings do not agree with calculated reflectances using existing optical constants at all wavelengths. We have calculated the magnitude and the direction of the shift in the optical constants of U and a-Si from reflectivity measurements of DC magnetron sputtered a-Si/U multilayers at 30.4 and 58.4 nm. The reflectivity of the multilayers were measured using a UV hollow cathode plasma light source, a 1 meter VUV monochromator, a back-thinned CCD camera, and a channeltron detector. These reflectance measurements were verified by measurements made at LBNL. The reflectances of the multilayer coatings were measured at 14.5 degrees from normal to the mirror surface. The optical constants were calculated using IMD which uses CURVEFIT to fit the optical constants to reflectivity measurements of a range of multilayer mirrors that varied over a span of 15.0-25.0 nm bilayer thickness. The effects of surface oxide and roughness, interdiffusion, and interfacial roughness were numerically subtracted in fitting the optical constants.

The δ, β determined at 30.4 nm does not well match the values of c-Si published in the literature (HBOC[1]), but do approach those of a-Si as reported in literature (HBOC). The difference in the optical constants of c-Si and a-Si are larger than can be attributed to differences in density. Why the optical constants of these two materials vary at 30.4 remains an open question.

Keywords: Optical Constants, Silicon, Uranium, EUV, VUV

INTRODUCTION

Optical constants are used to compute the response of a material to an interaction of light. Previously published optical constants for uranium and a-Si over portions of the extreme ultraviolet (EUV) are questionable. The optical constants of a-Si from peer reviewed literature[1,2] are not consistent with optical constants calculated from the atomic scattering factors of crystalline Si[3]. The optical constants for uranium and silicon predicted reflectances higher than we measured. Therefore, we have fit the optical constants of sputtered uranium and amorphous silicon using reflectance measurements.

Optical constants are important in the design of optical devices that may be used in multilayer optics, plasma diagnostics, lithography, and space optics. Specifically, we were involved in the design and fabrication of space flight mirrors for the IMAGE[4] explorer satellite. The proper design of these devices depends on reliably knowing the optical properties of many materials. It is also possible to learn about the basic electronic properties of a material by measuring its optical properties.

We used the optical constants of many materials to design multilayer mirror coatings for three cameras which were part of the IMAGE mission satellite. An iterative process was used to design the multilayer coating because the optical constants were not well known in the EUV. The multilayer samples that were made were used to obtain the optical constants of a-Si and U at 30.4 and 58.4 nm.. We were not certain if the individual optical properties of a-Si and uranium could be distinguished in a multilayer, but we were partially successful in the determination of the optical constants of a-Si and uranium in the EUV. Many different multilayers were prepared to understand the reflective properties of a-Si and uranium; we will only report on multilayers that have an a-Si/U Γ of 0.7±0.03 and have an uranium oxide overcoat.

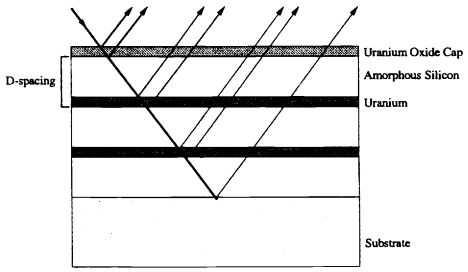


Figure 1. Example of a multilayer with a uranium oxide cap.

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OVERVIEW OF OPTICAL CONSTANT THEORIES

Classically, optical constant theories predict a simple relationship between the index of refraction of a material and its atomic density. The Drude theory is largely successful at estimating the optical constants by modeling the electrons as a gas[5]. In this model the optical constants, δ and β, scale linearly with atomic density. Therefore, the optical constants of compounds can be approximated by stochiometrically scaling the density of each element in the compound. This theory, obviously, does not work around optical absorption edges or at wavelengths where the energy of molecular bonds is on the same order as the energy that corresponds to the wavelength of the light. This paper will present data that shows atomic scattering factors do not work even at 41 eV in silicon, well above its molecular binding energies.

Quantum mechanics provides a rigorous model of how optical constants depend on the crystalline properties of a material and its density. The optical constants of a material are most sensitive to changes in density and bonding at energies that are of the same order of magnitude as the energies of the electrons involved in bonds. These more accurate models can be tied back to the Drude theory by using atomic scattering factors, which can be interpreted within the Drude model as the number of electrons each atom contributes to the electron gas. This assumption often permits one to scale computed optical constants with elemental density.

DEPOSITION AND CHARACTERIZATION WITH X-RAYS

The optical properties of uranium and a-Si were calculated from single angle (14.5° from normal) reflectance measurements of multilayer mirrors deposited via sputtering. Before sputtering begins, the deposition chamber is evacuated to about 10^{-6} torr to remove nitrogen, oxygen, and water vapor. This diminishes the incorporation of impurities in the deposited film that will change the optical properties of the materials being deposited. The partial pressures of water and nitrogen in the system are typically less than 10^{-6} torr before deposition. The partial pressures of all the gases in the deposition chamber are measured using a quadruple residual gas analyzer (RGA).

Deposition can begin after the base pressure in the chamber is 3×10^{-6} torr or lower. After the base pressure has been reached the entrance to the vacuum pump is mostly blocked or throttled. The pressure in the deposition chamber rises to $3\text{-}7 \times 10^{-6}$ torr after the entrance is throttled. Ultrahigh purity argon (99.999% pure) is then flowed into the system until the steady state pressure of about 10^{-3} torr is reached. The argon (Ar) pressure is maintained by mass flow controllers and is measured by the RGA.

The substrates are rotated over the target to increase the uniformity of the deposited material on the sample. The target is "masked" to increase the radial uniformity of the material on the sample. The shape and size of the masks are determined by an iterative process of measuring the spatial uniformity and then changing the masks.

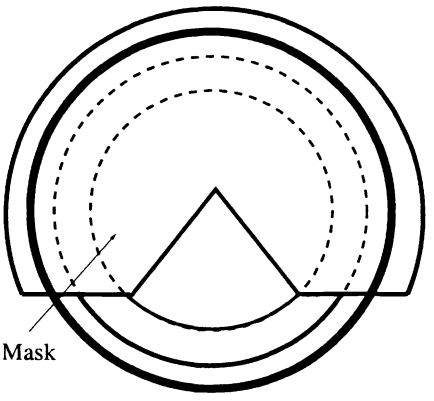


Figure 2. Top view of mask on top of sputter gun.

The thickness of each of the multilayer mirrors is determined by x-ray diffraction using a SCINTAG x-ray diffractometer at Cu kα. The thickness were determined by comparing the x-ray data to a model. The spatial uniformity in the radial direction is determined by measuring the thickness of a multilayer coating at various places on a sample. For the multilayers used in this paper a-Si is the top layer. The presence of the uranium oxide overcoat does not change the Γ of the a-Si/U multilayer.

The top layer of our multilayer mirrors is uranium, which readily oxidizes; 1.5 nm oxidizes in a few minutes when exposed to air . We found that having uranium oxide on the top of the multilayer increases the reflectance at 30.4 nm and decreases the reflectance at 58.4 nm. The apparent thicknesses of the uranium oxide layers are not the same for all of the multilayers. Many multilayers were made to determine the optimal thickness of the uranium capping layer. The approximate thickness of the uranium oxide layer was calculated by knowing the thickness of the pure uranium layer deposited in vacuum and then calculating the expansion of the uranium when it oxidized in air. Uranium expands at least 3.2:1 in volume when oxidized. Auger studies suggest the oxygen/uranium ratio in the surface oxide is 4:1.

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REFLECTANCE MEASUREMENTS AND ANALYSIS

We used a McPherson, model 225, 1-meter scanning monochromator to isolate one wavelength of light created in a plasma lamp. The light from the monochromator can be reflected off a mirror and into a detector, or the light can be directly measured to monitor the intensity of the plasma lamp. The detection chamber is pumped by a Varian 550 turbo molecular pump mounted directly behind the diffraction grating. The detector chambers are evacuated through the exit slits and by a separate Varian 300 turbo molecular pump to assure the detectors could be operated safely. The channeltron detector operates at a high electrical potential and would be destroyed by electrical arcing if operated above $1x10^{-4}$ torr.

A McPherson, model 629, hollow cathode plasma lamp is used to produce EUV light. The He pressure in the plasma lamp is measured by a Teledyne Hastings-Raydist DV-6M thermocouple gauge. Helium gas produces light at 58.4 and 30.4 nm. Neutral He has two electrons in the 1s shell. When an electron is excited to the 2p state and decays to the 1s state it will radiate light at 58.4 nm. This is a very intense spectral line because it does not need a lot of energy to be excited, the helium atom does not have to be ionized, and the 2p→1s is a probable transition. The 30.4 nm line is created by the 2p→1s transition in a singly-ionized helium atom. This spectral line is not as bright as 58.4 nm because of the optical efficiency of the monochromator and detector are less at 30.4 nm. It also depends on the percent ionization of the helium gas. The hollow cathode source was run in series with a 2000Ω ballast resistor to limit the current in the lamp.

The McPherson scanning monochromator is used to select a specific spectral wavelength of light. The McPherson monochromator can also scan smoothly through many wavelengths making it possible to measure the reflectivity of a sample over a range of frequencies of light. The monochromator can isolate light from about 30.0 to 100.0 nm, and select with an accuracy of about 0.05 nm. Our platinum-coated grating reflects about 12% of the light between 30.00 and 60.0 nm.

The principally unpolarized beam of light reaching the sample is defined by adjustable entrance and exit slits. The vertical slits are 50-300 microns depending on the intensity of the light. The horizontal slits are normally 0.5 centimeter in width, and were infrequently changed.

MEASUREMENT CHAMBERS

Two chambers were used to measure the reflectances of multilayer coatings. Chamber 1 was used to measure absolute reflectivity. It can only measure the reflectivity of one mirror coating at a time. Chamber 2 is used to measure the reflectivity of three mirrors relative to a known reference mirror. Using Chamber 2, we could make reflectance measurements significantly faster than using Chamber 1. Both chambers were designed to measure the reflectance of mirrors at 14.5° relative to normal to satisfy the requirements for the IMAGE mission mirrors.

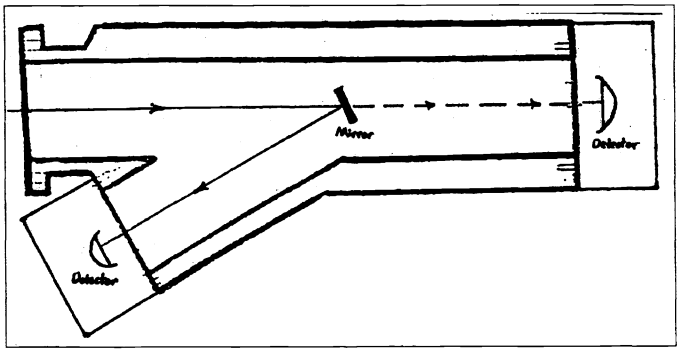


Figure 3. Chamber 1

Absolute reflectances can be measured using Chamber 1 because the intensity of the source and the intensity of the light coming off a mirror can be measured by the same detector. The distance from the exit slits to the back of chamber is the same as the total distance from the exit slits to the mirror to the side of the chamber. These two distances are important because the light coming from the exit slit diverges. Measurements are made by attaching the detector to the back of chamber 1and measuring the intensity of light. The detector is then moved to the side of Chamber 1 and a mirror is put in the center of the beam. The intensity of the light reflected from the mirror is measured. The mirror is removed, and the detector is put on the back again to check the stability of the source. This process is repeated several times because the source changes with time.

Chamber 2 was designed to measure the reflectivity of the curved mirrors for the IMAGE mission. The reflectivity of flat samples could be measured with a special holder that was designed to hold four flat mirrors at the same angle and position as a curved mirror would be in Chamber 2. Because of the design it is very easy to measure the reflectances of the other

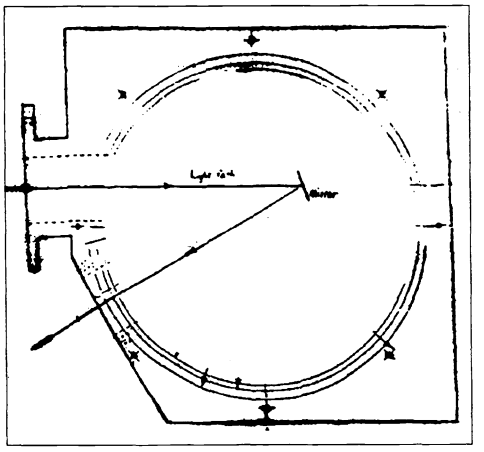


Figure 4. Chamber 2

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three mirrors relative to reference mirror of a known reflectivity. Only one sample needs to be aligned because the mirror holder was machined from one piece of aluminum and the sample positions are fixed. The relative alignment of the sample positions has been verified and is not a significant source of error.

DETECTORS

During different phases of research either one of two detectors was used to measure the intensity of the light coming from the monochromator and reflecting off the mirrors. A CCD camera is used to image the spatial variations in the plasma source and to check the alignment of the mirrors in the chambers. A channeltron detector is used in the majority of the measurements because it is more sensitive than the CCD camera.

The CCD camera is a Princeton Instruments back-thinned CCD camera with 512x512 pixels in a 1.25 cm square active surface optimized for detection in the EUV. The benefit of using a CCD camera is its ability to produce an image. This is important because the plasma source discharge is not spatially uniform and it is important to know the shape of the plasma at different wavelengths. There are, however, some disadvantages in using the CCD camera: the camera is not as sensitive as the channeltron, the camera must be cooled to -50 °C, and the chip surface is very delicate.

The channeltron detector is an AmpTek model MD-501. The channeltron detector has a background count of less than a half count per second. This background is ignored in all measurements because usual measurements average several thousand counts a second. The channeltron is used for the majority of the measurements because the data collection is significantly faster than the CCD camera, there is a small background, and the detector does not need to be cooled. The main disadvantages of using the channeltron detector are that it must be operated below 10^{-4} torr and it does not image.

MEASUREMENTS AND DATA ANALYSIS

Most of the measurements were made using Chamber 2 by aligning a sputtered molybdenum reference mirror (measured with Chamber 1) so the greatest amount of counts was reflected from the mirror at a given wavelength. The intensity reflecting from the reference mirror was recorded two or three times to monitor the stability of the plasma lamp. The other samples were then moved into the beam and the intensities of the three samples were recorded two or three times. The reference mirror was measured again to monitor the long-term stability. This process was repeated several times to record the variations in the source, but did not give a measure of the time variations of the source.

The raw data taken from the mirrors gave a range of reflectances for each mirror. There were normal statistical variations because the detectors counted a certain number of photons in a fixed time. There were variations in the deposition of the multilayer mirror coatings and the thickness of the uranium oxide, making each coating be slightly different. Also, the reflectance is sensitive to surface contaminants. There were variations in the measurement of the reflectances. The plasma lamp was unstable and each mirror may have been aligned slightly different.

These variations can be classified as statistical and experimental error[6]. The majority of the error was experimental, because of the limitations inherent in the measurement chambers. The statistical error was a small factor in the error. The statistical error was reduced by lengthening the exposure time so the statistical error is about 1%. The statistical methods used in the data reduction are furthered explained in reference 7.

DATA AT 30.4 AND 58.4 NM

All the mirror coatings consisted of seven periods of a-Si on uranium with $\Gamma=0.7\pm0.03$ over a range of d-spacings from 15.0-27.0 nm. These multilayers had an uranium oxide overcoat on top of the seven periods of a-Si and uranium bilayers. All the mirrors were measured at 14.5° from normal. All the mirrors were measured multiple times, but some measurements were more reliable than others and were so weighted. The error bars (Figures 5,6) were calculated by the methods explained in reference 7.

CALCULATED REFLECTANCE IS DIFFERENT THAN MEASURED REFLECTANCE

At 30.4 nm (Figure 5) the measured reflectivity peak position, relative to the calculated peak, is shifted 0.5 nm towards a higher layer thickness. The calculated refractive indices of uranium and a-Si are both closer to unity (Table 1). The shift in the peak position and the shift in the fitted optical constants are self consistent. We are investigating the interdiffusion of the uranium and a-Si layers and the oxidation of uranium and a-Si to explain differences in the reflectances of these multilayer mirrors.

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At 58.4 nm (Figure 6), the shape of the reflectivity versus period curve can be approximated by a straight line. This is not unexpected because the multilayers were designed to have a broad minimum around 58.4 nm, however the reflectivity is significantly lower than the calculated reflectivity. Both roughness and surface oxidation can lower reflectance. However, the reflectance is much lower than could be expected if roughness were the only factor affecting the reflectivity. Longer wavelength light (i.e. 58.4 nm) is scattered less by roughness than shorter wavelength light (i.e. 30.4 nm). It is well known that the effect of roughness is to decrease the reflectance of a surface at shorter wavelengths more than at longer wavelengths. Thus, even if the roughness in the multilayers was more than seen in TEM[8] in our calculations it would have lowered the reflectivity at 30.4 nm much more than at 58.4 nm. This is not seen. Multilayers capped with uranium oxide are between 1/2 to 1/3 less reflecting at 58.4 nm than would be expected. No decrease is seen in the reflectance at 30.4 nm, but an increase is seen in the reflectance as a result of the presence uranium oxide layer on top of the last a-Si layer. We conclude that the lowering of the reflectance at 58.4 nm is caused by the presence of the uranium oxide layer, rather than roughness or a deviation from the published optical constants of a-Si and uranium at 58.4 nm[7].

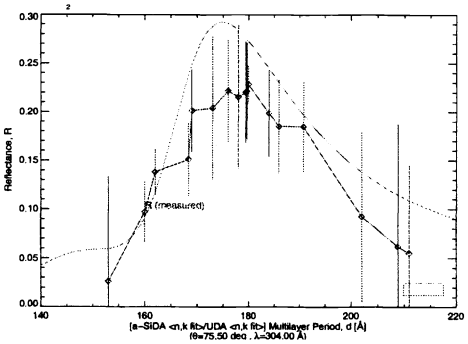


Figure 5. Calculated vs Measured Reflectance at 30.4 nm

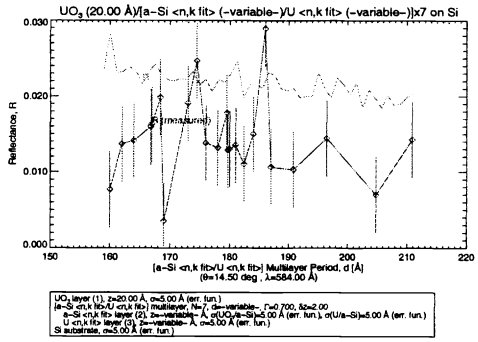


Figure 6. Calculated vs Measured Reflectance at 58.4 nm

The relative difference between measurement and modeled reflectances at 58.4 nm is more pronounced than at 30.4 nm. This shows the current understanding of optical constants of a-Si, uranium, and compounds like uranium oxide in the lower to middle EUV is deficient. This might be expected because 58.4 nm (21eV) is a lower energy then 30.4 nm (41eV), and would be more affected by the atomic bonding of the materials in a multilayer. The closer the energy of the light is to the energy of the bonds in the material the stronger the effect on the optical constants.

CALCULATED OPTICAL CONSTANTS

The measured reflectances were used to calculate the optical constants of uranium and a-Si by fitting a model of the multilayer to the measured data points. IMD[10] was used to fit the optical constants to the measured data. IMD used CURVEFIT and the Marquardt method of non-linear least squares fitting[5]. The surface and interfacial roughness was set to 0.5 nm based on other measurements[8].

To fit the optical constants with IMD, a model of the multilayer mirror, initial values of the parameter to be fit, and the measured data are entered into IMD. The number of fitting parameters that can be chosen depends on the number of data points. More fitting parameters can be used if there are more data points, but experience has shown that care must be taken to avoid over-fitting a physical feature with extraneous nonphysical parameters. IMD can be used calculate the confidence interval over a user-defined grid space to determine the goodness of the fit.

We chose the initial values of δ and k for silicon to be close to the values of crystalline silicon, and the values of uranium close to those reported in reference[9]. The confidence integral was not conclusive for the fit optical constants of uranium, so the error bars of these fits are not reported. The literature values and the best fits to date are shown in Table 1.

		30.4 nm		58.4 nm
	Material	δ	β	δ
Literature Values (approx. original values)	c-Si[1]	0.063	0.009	0.373
	U[9]	0.322	0.279	0.41

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Fit Values	Sputtered Si	0.039 ±0.025	0.037 ±0.015	Not Fit
	Sputtered U	0.306	0.067	0.51
Literature Values	a-Si[1]	0.027	0.0314	0.215

Table 1. Optical Constants of literature and fit values for uranium and silicon.

The magnitude and direction of the shifts in δ and k for a-Si and uranium are noteworthy at both 30.4 and 58.4 nm. The largest changes are in k. The k of a-Si increased about four times, while the k of uranium decreased about four times. The δ of uranium changes little while the δ of sputtered Si is about half that of crystalline Si. It is instructive to compare the fit optical constants of silicon with the published values of a-Si (bottom row of Table 1). The fit δ and k are closer to the literature values of a-Si than to the literature values of crystalline silicon. This supports the need to measure the optical properties of sputtered silicon, but leaves open the basic question. Why do the optical properties of crystalline and amorphous Si differ at all? The observed differences are much larger than can be accounted for on the differences in density of the two materials. The major difference is atomic packing, that is, the density of the material. The standard model for calculating optical constants, at or near x-ray energies, weights each by the ratio of the density of the material in the multilayer to its standard density. This ratio is about 0.8 for room temperature sputtered amorphous silicon. The fact that the optical constants of a-Si differ so much from the optical constants of c-Si demonstrates the inadequacy of this model in the EUV. But why the model fails in not clear.

CONCLUSIONS

We have determined the optical constants of uranium and a-Si and 30.4 and 58.4 nm using reflectance measurements of multilayer mirror coatings. The change in k at 30.4 nm is large and is significant. The changes in δ are smaller, but are still significant. The changes in the optical constants at 58.4 nm is probably significant but the data does not support strong conclusions. The large differences between the measured and calculated reflectance is noteworthy. The top layer of uranium oxide plays a stronger role in the reflective properties of 58.4 than anticipated. The effects of the oxide layer could be eliminated by an ultrahigh vacuum system that is capable of deposition and measurement without exposure to water vapor, oxygen and nitrogen. Measuring the optical constants of uranium oxide in the EUV also has merit.

Our effort to determine optical constants based on multilayer reflectance was only partially successful. A greater span of Γ, and angles of measurement would have helped. Independent measurements of layer interdiffusion, roughness, and material composition would help set limits of what the optical constants of a material are. It would be helpful to measure the reflectivity of a single film or layer pair to obtain the optical constants of a material to better isolate the properties of one material.

We are building a chamber that will measure reflectivity of a sample as a function of angle, ultimately we expect to be able to do in situ deposition of thin films. An EUV ellipsometer is being developed at BYU and will provide another means to measure the optical properties of materials in the EUV. The development of a more robust fitting algorithm will also be an important step to accurately determine the optical constants of materials in the EUV.

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