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The optical constants of gallium stabilized δ-plutonium metal between 0.7 and 4.3 eV measured by spectroscopic ellipsometry using a double-windowed experimental chamber

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Abstract

A double-windowed vacuum-tight experimental chamber was developed, and calibrated on the spectroscopic ellipsometer over the energy range from 0.7 to 4.5 eV using a silicon wafer with an oxide layer of approximately 25 nm to remove the multiple-window effects from measurements. The plutonium sample (3 mm diameter, 0.1 mm thick) was electro-polished and mounted into the sample chamber in a glove box having a nitrogen atmosphere with less than 100 ppm moisture and oxygen content. The index of refraction n and the extinction coefficient k decrease from 3.7 to 1 and 5.5 to 1.1, respectively as the photon energy increases from 0.7 to 4.3 eV.

Keywords: Plutonium; Uranium; Optical constants; n; k; Ellipsometry

1. Introduction

The optical constants of plutonium metal are of scientific interest because of their relationship to the electronic structure of the material [1]. They are of practical interest to the nuclear industry because they need to be known before ellipsometric measurements of plutonium oxidation can be interpreted. They have so far been measured only at single wavelengths, i.e. for the solid metal at 5461 Å [2] and for the liquid metal at 6328 Å [3]. Such measurements have in the past only been made inside special facilities because the material is highly radioactive and oxidizes quickly in air; we made them instead in an ordinary laboratory environment by using only a small quantity in a double-walled container.

2. Experimental

2.1. Design of the experimental chamber

The double-windowed experimental chamber has to fulfill three requirements: (1) safety regulations necessitate that all openings have two independent seals, (2) reproducibility of ellipsometry demands that the entering and exiting photon beams are always normal to the glass surfaces, and pass them always at the same spot, (3) avoiding oxidation necessitates that the seals be vacuum tight, so that the sample can be maintained in an inert atmosphere while the measurements are being made. Item 2 is fulfilled by always fitting the chamber onto the ellipsometer's working platform into the same position and orientation. Good vacuum seals on all windows meet requirements 1 and 3. Fig. 1 shows an exploded view of the chamber that fulfills all requirements. Its body is machined from a solid aluminum block. It has three openings for windows, and one to introduce the sample. The first set of windows in each opening is sealed to the body with an epoxy known to have good vacuum properties [4]; the second set of windows is sealed with O-rings. The windows are arranged such that the photon beam can enter or exit either normal to the target, or at an angle of 65° with respect to the target's normal. All windows (UV-grade fused silica) are seated flat on the machined surfaces and are subjected to minimal stress. The sample holder is sealed to the bloc using an O-ring. It is machined such that it fits tightly into the bloc and that the target surface is located exactly at the intersection of the centerlines of the three windows. At the back of the sample holder is a circular hole. The second flange following the sample holder is again sealed to the bloc with an O-ring, and has alignment pins on both sides, and a recess on the backside. The alignment pin on the front side fits tightly into the hole at the sample holder, and the alignment pin on the backside fits tightly into a centering hole on the ellipsometer's work platform. The platform has two additional holes connected to a vacuum pump and concentric with that centering hole; they evacuate the recess on the backside and hold the experimental chamber securely but allow rotation of the chamber so that the flat faces of the aluminum block can be aligned parallel to the ellipsometer's work platform. All windows consisted of UV-grade fused silica.

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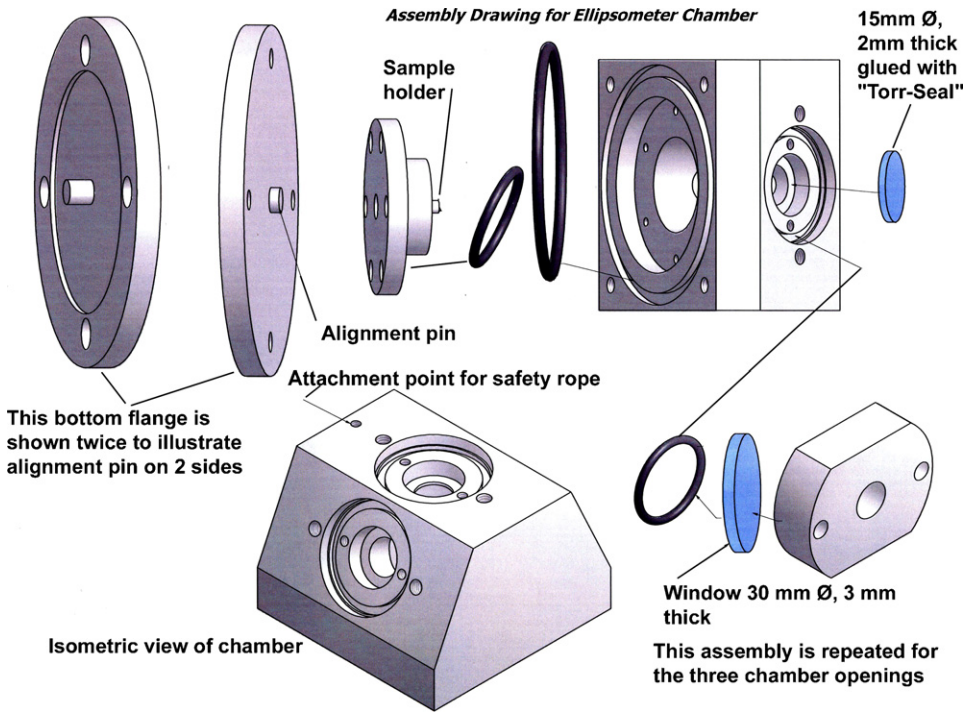

Fig. 1. Assembly drawing of double-windowed ellipsometer chamber for plutonium analysis.

2.2. Calibration of the chamber to eliminate window effects

The vector representing the photon beam is affected not only by the sample itself, but also by passage through four windows. To determine the window effects one measures over the photon energy range of interest the ellipsometric response of a small silicon wafer sample having a surface oxide layer with a thickness of ~25 nm mounted first in air and then in the experimental chamber. From these different responses a transfer function is derived that is then applied to correct the response from unknown samples. A commercial company supplied the ellipsometer and the software used for all calculations [5]. Fig. 2 shows the values of Δ and Ψ measured in air fitted to a model consisting of bulk silicon, a 1 nm thick Si/SiO_2 interface layer, and a silicon dioxide layer of adjustable thickness. The best fit gives a Si/SiO_2 thickness of 25.5 nm. Fig. 3 shows the values of Δ and Ψ obtained on the same sample mounted in the chamber after the window correction was applied. These values were again fitted to the same model. The best fit gives a SiO_2 thickness of 25.8 nm. Figs. 2 and 3 demonstrate that the window correction function eliminates the window effects with sufficient accuracy.

2.3. Plutonium sample characterization and preparation

The material used was gallium stabilized delta phase plutonium. The sample started out as a disk of 3 mm diameter with a thickness of less than 1 mm. The sample was mounted on a lapping fixture with low temperature melting wax. The first side was lapped until a thickness ≈200 μm was reached using 30, 12, 3 μm abrasive paper, and finished with 1 μm Al_2O_3 lapping paper. The sample was un-mounted, turned over and again lapped with the same succession of lapping films to a 1 μm finish until the thickness of the discshaped sample was 101 ± 1 μm thick. The sample was annealed on a hot plate for 10 min at 150 °C

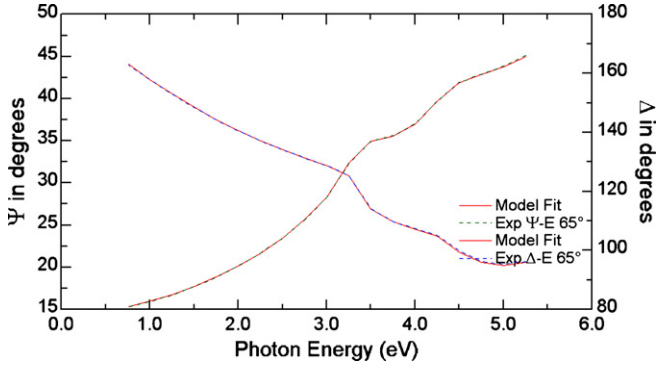

Fig. 2. Experimental data Δ and Ψ measured in air on a 1 cm^2 oxidized silicon wafer. A model consisting of bulk silicon, a 1 nm thick Si/SiO_2 interface layer and a SiO_2 layer of adjustable thickness provides the best fit at a SiO_2 thickness of 25.5 nm. Data are taken at 50 meV intervals, too many to be individually displayed. There is no detectable difference between data (dashed blue line) and model fit (continuous red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

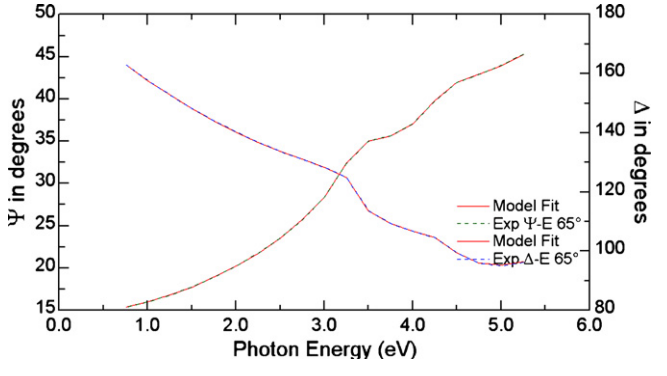

Fig. 3. Experimental data Δ and Ψ measured on a 1 cm^2 oxidized silicon wafer mounted in the experimental chamber after correcting for window effects. A model consisting of bulk silicon, a 1 nm thick Si/SiO_2 interface layer and a SiO_2 layer of adjustable thickness yields the best fit at a SiO_2 thickness of 25.8 nm. Data are taken at 50 meV intervals, too many to be individually displayed. There is no detectable difference between data (dashed blue line) and model fit (continuous red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

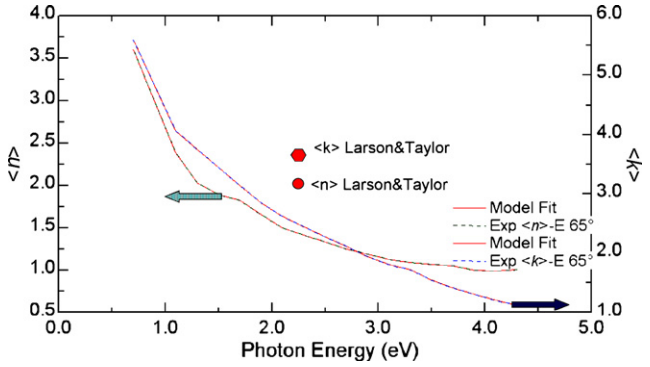

Fig. 4. Index of diffraction n and extinction coefficient k of plutonium metal with an oxide thickness of a few nm. Data are taken at 50 meV intervals, too many to be individually displayed. There is no detectable difference between data (dashed blue line) and model fit (continuous red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

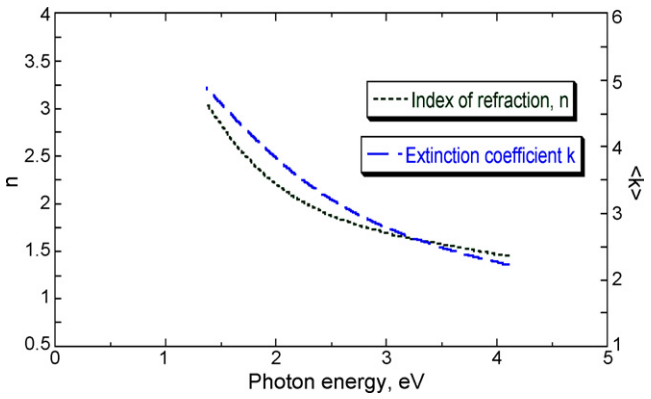

Fig. 5. Index of diffraction n and extinction coefficient k of uranium metal. Data are taken at 50 meV intervals, too many to be individually displayed. There is no detectable difference between data (dashed blue line) and model fit (continuous red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

in order to revert any alpha phase that may have formed from the mechanical polishing. The sample was then electro-polished for 5 s, removing ≈2 μm of metal leaving a surface that appeared highly polished to the naked eye. The sample roughness is estimated to be less then 5 μm and the parallelism to be 10 μm over 3 mm. The electro-polishing solution is 10% nitric acid, 45% ethanol, 45% butoxyethanol, used at −12 °C, and the polishing voltage is 135 V. Under these conditions the typical removal rate is ≈0.3 μm/s. All work is done in a N_2 glove box with O_2 and H_2O below 100 ppm. The sample was glued onto the experimental chamber's sample holder and sealed in said chamber inside the glove box. The sample was analyzed on the ellipsometer after approximately 20 h in the experimental chamber. Transmission electron microscopy on thin samples prepared in this manner and analyzed after having been held for a day in the glove box atmosphere show an oxide thickness of a few nanometres.

3. Results

The measured Δ and Ψ (corrected for window effects) were fitted to a Drude model [6]. In a Drude model the optical properties are derived by treating the metal as a free electron gas in which the electrons have a randomized velocity distribution and move according to Newton's laws between instantaneous scattering events [7]. A Drude model for gold provided the starting values for the optical constants ultimately determined. The ellipsometer's software was used to modify the model parameters of gold and to derive the optical constants n and k that are shown in Fig. 4 together with the model fit.

4. Discussion

In Fig. 4 our $\langle n \rangle$ and $\langle k \rangle$ data are plotted together with the data of Larson and Taylor at 546.1 nm (∼2.27 eV). The two data sets differ substantially at 2.27 eV. This difference may be due to several factors: (1) Larson and Taylor do not mention any correction for the two Pyrex windows in the light path of the ellipsometer. (2) The two surfaces are different: Larson and Taylor's surface is roughened by argon ion sputter cleaning in an ultrahigh vacuum system, while the surface used in this work was electro-polished and held in a nitrogen atmosphere with O_2 and H_2O below 100 ppm. Though oxidation of Ga stabilized ∂-plutonium is slow [8], an oxide layer of a few nm thickness has been observed by transmission electron microscopy of samples prepared in this manner. This thin oxide layer may effect the results reported here. The optical constants of uranium metal have been measured with the same instrument without the 65° chamber, albeit over a smaller range of energies. They are depicted in Fig. 5. Comparison of Figs. 4 and 5 shows that plutonium has a lower extinction coefficient and index of refraction over the range energies where comparison can be made. These differences are related to the differences intraband and interband electronic transitions occurring in these materials, and to our knowledge have not been derived and predicted from first principle calculations. The plutonium data acquired here will be used to model the ellipsometric response of an oxide covered plutonium surface and to determine the optical constants of surface oxides of plutonium.

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