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The optical properties of a polished uranium surface and its epitaxial oxide, and the rate of oxide growth determined by spectrophotometry

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ABSTRACT

Wide-band reflectrometry and ellipsometry have been used to determine the optical properties n and k of freshly polished uranium and of the epitaxial oxide layer, and also the rate of oxide growth in air. Results for uranium metal as well as for epitaxial oxide are compared with single wavelength ellipsometry literature values.

INTRODUCTION

The thickness of the oxide layer grown in air on the surface of uranium is of interest to the nuclear industry. To determine it, one must know the optical constants of the underlying uranium substrate and of the oxide layer. The optical constants n(refractive index) and k(extinction coefficient) at a fixed wavelength of 546.1 nm have been evaluated in a review of preceding work to be (n=3.1, k=3.9) for uranium, and (n=2.2, k=.5) for the oxide grown on a uranium substrate [1]. The dielectric constants (and hence n and k) of single crystal UO_2 have been measured over a wide range of energies [2,3]. However, the surface oxide grown in air on a uranium substrate is not single crystal UO_2 but shows Raman peaks of diverse oxide moieties [4] and hence the constants derived in [2,3] do not quite apply. The optical properties of the metal over a wide wavelength range can be determined accurately only by generating and holding the atomically clean sample surface in an ultra high vacuum, since uranium oxidizes rapidly. We use reflectrometry which can collect data quickly after polishing to collect data from a surface with a minimal oxide layer. Usually ellipsometry is used to measure properties of surface layers, here we apply both reflectrometry and ellipsometry to compare both techniques.

EXPERIMENTAL DETAILS

A uranium sample with a total weight impurity content of approximately 150 ppm was mechanically polished, finishing with 1μm SiO_2 particles. The sample surface was analyzed a few seconds after polishing by a commercial reflectrometer (n&k 1700, n&k Technology Inc., Santa Clara, CA 95054) over a spectral range from 200 to 900 nm. The incident and reflected light were close to surface normal, and since data collection time was about a second, the effect of surface oxide on optical response was minimized. The same sample was analyzed subsequently by a commercial variable angle spectroscopic ellipsometer with a wide spectral range (193-2200 nm) (VASE, J.A. Woolam Co., Inc. Lincoln, Nebraska 68508) at 65, 70, and 75 degrees angle of incidence. The ellipsometry measurements require more time, and hence the first ellipsometry data contain a larger contribution of the surface oxide.

DISCUSSION

Optical constants of Uranium and Uranium surface oxide

Reflectance data for the metal were processed using the Cauchy dispersion relation and for the oxide by relying on Forouhi-Bloomer analysis [5,6]. Excellent agreement between measurement and analysis was found for uranium immediately after polishing and for oxide covered uranium, see figure 1.

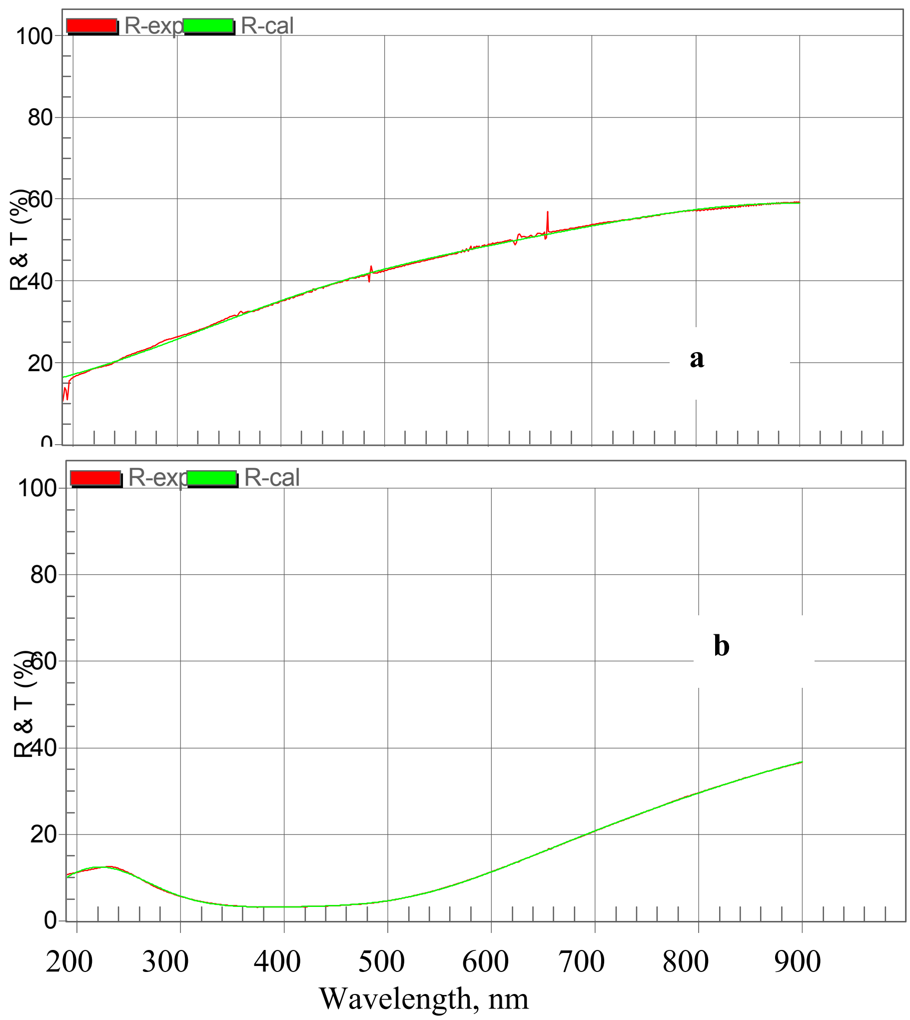

Figure 1. Experimental and calculated reflectance R as a function of wavelength of an uranium surface **a)** after approximately ten seconds exposure to laboratory air, **b)** with an oxide layer approximately 28nm thick.

Bare metal reflectance at 632 nm is .5, see figure 1a. Ellipsometry data (Δ and Ψ at 65°, 70° and 75°) were analyzed by initially fitting the first measurements made after polishing to a Cauchy metal model only, secondly fitting the last measurement made on the oxidized sample to a model consisting of the uranium metal plus an oxide layer, the optical response of the oxide layer being represented by three Gaussian oscillators, thirdly refining the metal model by fitting the first measurement made to a model consisting of metal covered with a thin oxide represented by the oscillators defined in the second step. In a fourth and final step the oxide model was refined by reanalyzing the last measurement made as consisting of a metal substrate having the optical characteristics derived in the third step and adjusting the parameters of the three Gaussian oscillators. The end result of the analysis fit Δ and Ψ of the last measurement very well, see figure 2, and Δ and Ψ of the first measurement less well. Ellipsometry provides 6 data points to fit at each wavelength and is therefore much more difficult to fit exactly than reflectometry

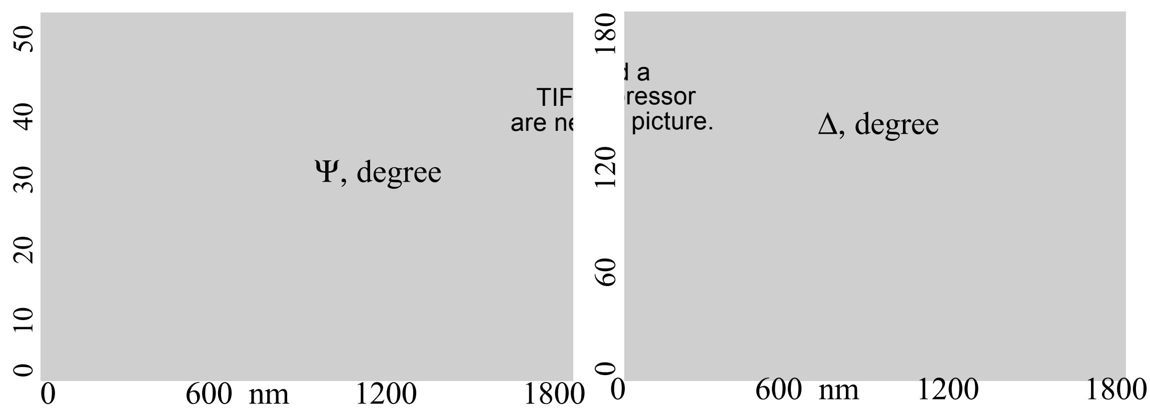

Figure 2. Ellipsometry data and fit for a 73 nm thick oxide layer on uranium.

Figure 3 shows a comparison of n and k for uranium metal deduced from reflectometry and from ellipsometry. In addition n and k at 546 nm from [1] are plotted. Both n and k deduced from reflectometry are substantially smaller over the whole wavelength range than n and k from ellipsometry done on this sample. The value of k reported by [1] is close to the value determined by ellipsometry in this experiment, while [1]'s value of n is higher than any value measured here by either technique over the whole wavelength range. In contrast, n and k measured by either ellipsometry or reflectometry for the surface oxide on uranium metal, shown in figure 4, are close to each other, and close to literature values [1]. The reflectometry values for n and k are again consistently smaller than ellipsometry's. These two analysis techniques rely on parameter fits to different models of the optical response of uranium oxide to the experimentally measured values and can both fit those well. However, ellipsometry measures a wider range of parameter and is generally accepted as the standard. The absorption coefficient at 632 nm, a typical wavelength for Raman spectroscopy, is approximately .01 nm^{-1} indicating that optical analysis of the oxide's properties can be performed on oxides with about 100nm thickness.

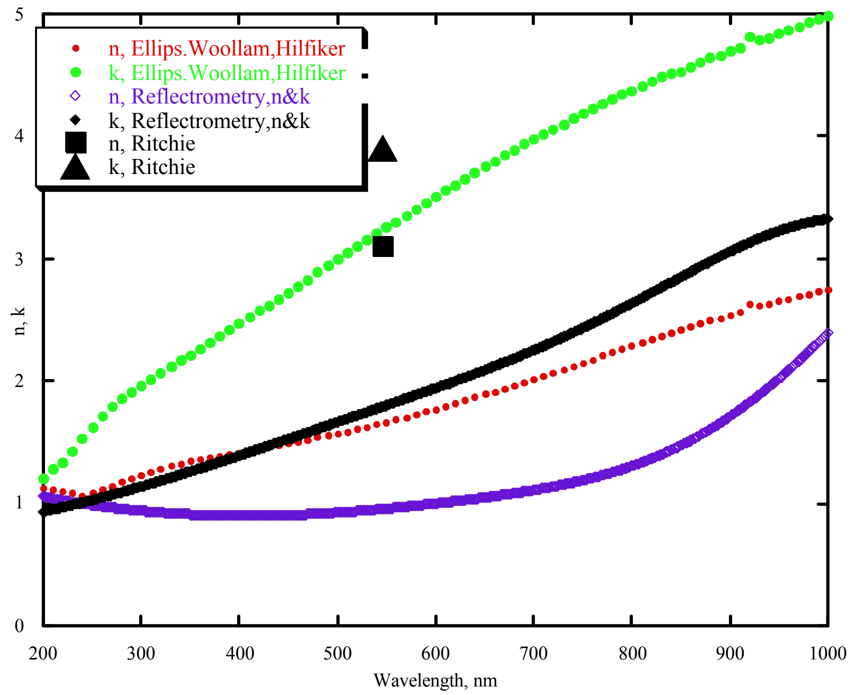

Figure 3. The optical constants n and k of bare uranium as a function of wavelength deduced from ellipsometry and reflectrometry, and literature values of n and k at 546 nm.

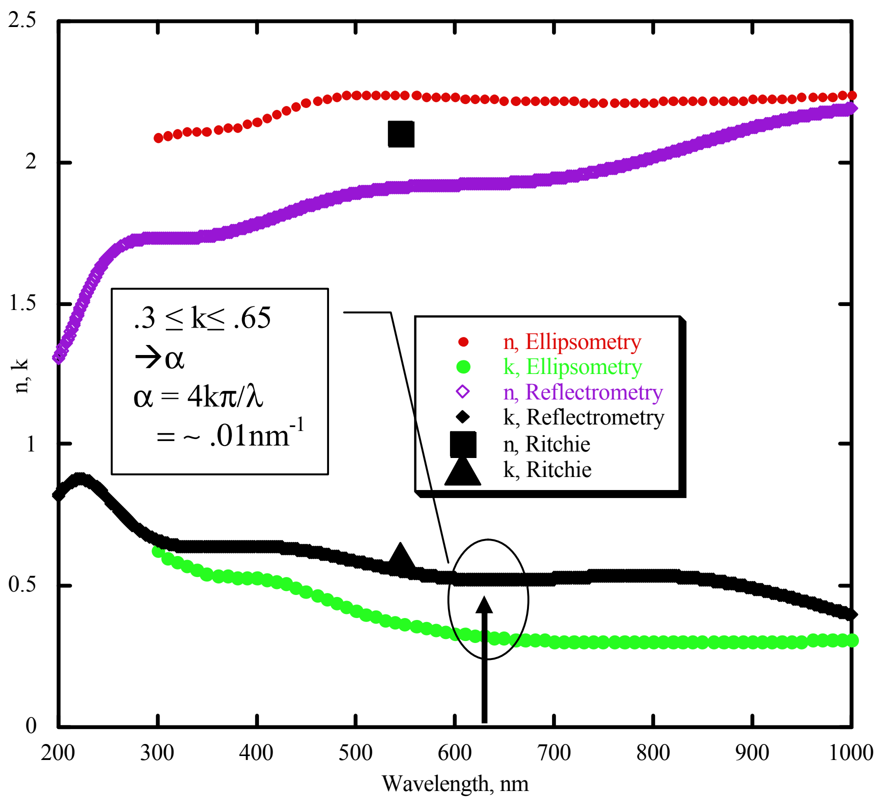

Figure 4. The optical constants n and k of surface uranium oxide as a function of wavelength deduced from ellipsometry and reflectrometry, and literature values of n and k at 546 nm.

Oxide growth kinetics.

The fitting process for both ellipsometry and reflectrometry yields the oxide thickness in addition to the optical parameters. In figure 4 reflectrometry's thickness data are shown on a double logarithmic plot as a function of time in minutes, since reflectometry can quickly acquire data. The overall growth is well described by a diffusion controlled (~time$^{.5}$) model, even though the first 10 minute's data may be better fit by an exponent greater than one half.

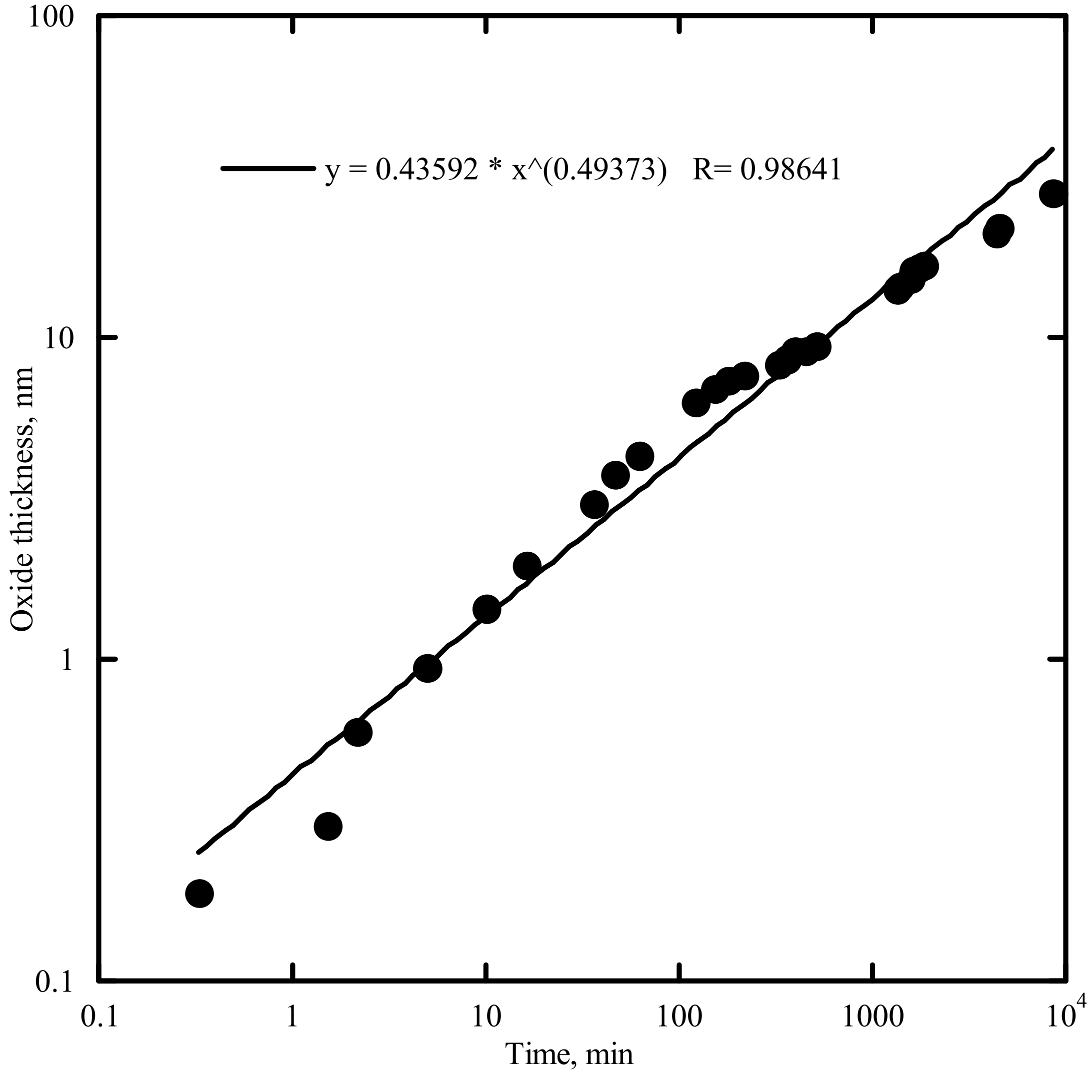

Figure 5. Uranium oxide growth kinetics determined by reflectrometry.

In figure 6 the deduced thickness of both reflectrometry and ellipsometry are shown on a double logarithmic plot as a function of square root of time. The first data points for ellipsometry were lost.

The data from these two techniques appear to be consistent with each other. The power exponent of the fit to √time is, however, not one and the growth of both the reflectrometry data (open squares) and the ellipsometry data (open squares with a solid square in its center) appears to decrease with time. The oxide growth is close to that determined by diffuse reflectance infrared spectroscopy, adjusted for the difference in laboratory temperature [7].

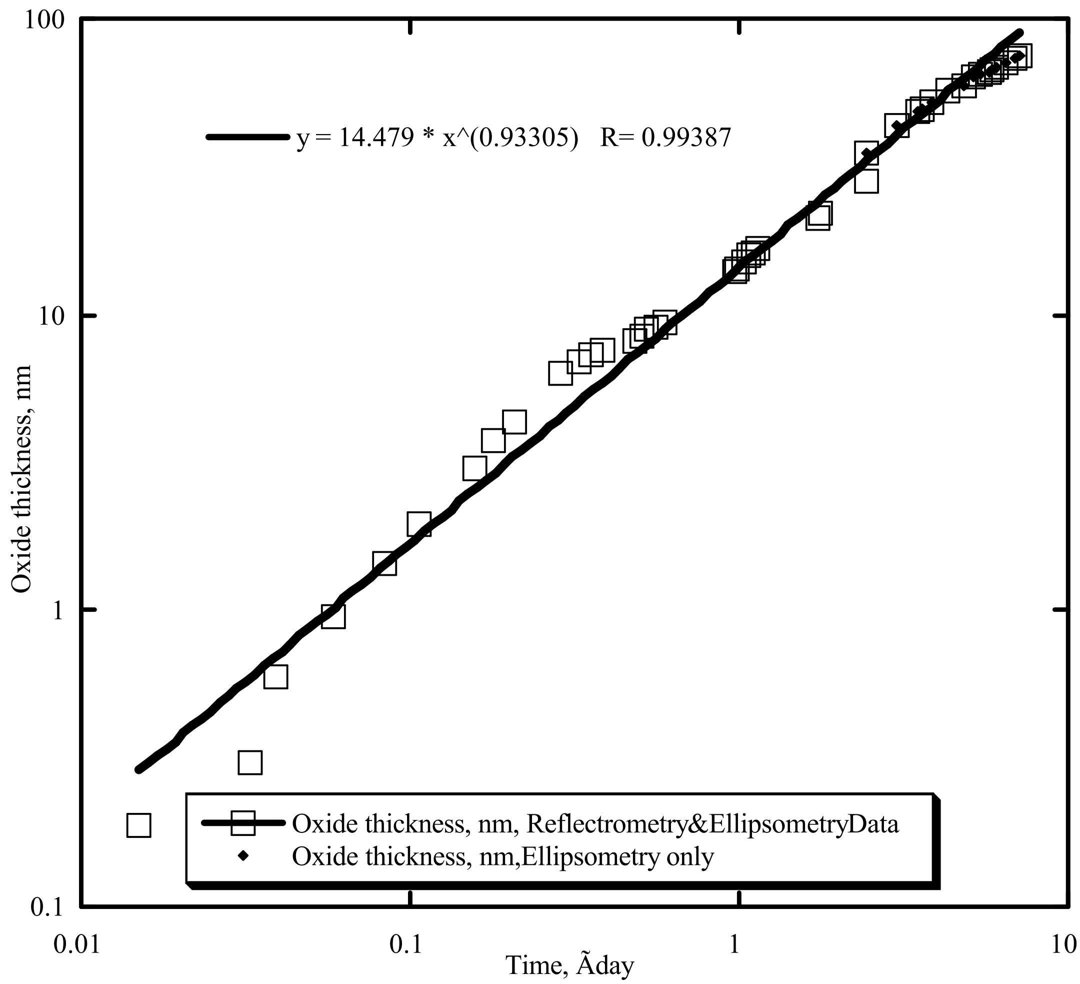

Figure 6. Uranium oxide growth data measured by both reflectrometry and ellipsometry.

CONCLUSION

Reflectrometry and ellipsometry lead to oxide growth measurements consistent with each other, even though the optical properties of the oxide determined by the two techniques differ somewhat from each other and from literature values at 546 nm, despite the fact that employ models that promise to be consistent with the Kramers-Koenig relationship. The two techniques differ strongly from each other and from literature values in the optical properties of the uranium substrate, possibly because a uranium surface polished in air has properties that differ from a sputter-cleaned or vapor-deposited surface in ultrahigh vacuum. The reflectrometer used here has a much shorter data acquisition time (seconds) and a smaller spot size (as small as 15 μm), making it possible to acquire oxide data immediately after polishing.

ACKNOWLEDGMENTS

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