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CHARACTERISTICS OF URANIUM OXIDES
PRODUCED BY THERMAL AND OXYGEN-
ION BOMBARDMENT REACTIONS

THE DOW CHEMICAL COMPANY
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U.S. ATOMIC ENERGY COMMISSION
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CHARACTERISTICS OF URANIUM OXIDES PRODUCED BY THERMAL AND OXYGEN-ION BOMBARDMENT REACTIONS

Donelly T. Larson, Norman W. Taylor, and Kazuji Terada

Abstract. The characteristics of oxides prepared on uranium by thermal and oxygen-ion bombardment reactions at 50° and 100°C were observed utilizing ellipsometry, high energy electron diffraction (HEED), and x-ray diffraction techniques. For each oxide prepared, oxide thickness as a function of time was observed. The index of refraction at 5461 angstroms (Å) determined from ellipsometer measurements of the thermal oxide is (2.5 – 0.5i); and the index of refraction for the ion-bombardment oxide is (2.5 – 0.4i). The oxides produced by ion bombardment were less crystalline than those produced thermally.

INTRODUCTION

Adherent oxides may be prepared on metal surfaces by exposing the metal surface to an oxygen environment or by oxygen-ion bombardment. The characteristics and properties of these oxides are not well known. There is evidence that the properties of thermal and ion-bombardment oxides will be different.

Newkirk and Martin (1)* observed that uranium which was inert-gas ion bombarded had a slower oxidation rate in air than uranium which was abrasively polished. They determined that the inert-gas ion bombarded uranium had an amorphous oxide layer, while the abrasively polished uranium had a crystalline oxide layer. The slower oxidation rate was attributed to the presence of the amorphous oxide surface layer which inhibited the diffusion of uranium atoms from the metal lattice to the oxide-air interface. The amorphous oxide in this case served as a protective barrier against further oxidation.

The properties and possible differences between thermal and ion-bombardment oxides were investigated utilizing ellipsometry, high energy electron diffraction (HEED), and x-ray diffraction techniques. Ellipsometer measurements *in situ* provided information on thickness as a function of time and on the optical properties of the oxides. High energy electron diffraction (HEED) and x-ray diffraction measurements determined the structure and state of crystallinity. The thermal

and oxygen-ion bombardment oxides were prepared on uranium surfaces.

Experimental Methods:

A. APPARATUS – The experimental apparatus used in the ellipsometer studies was essentially the same as reported in a previous paper (2). Some modifications of the sample chamber were made, however, to facilitate the positioning of the metal sample in the light beam. The sample was suspended by an electrically insulated rod which could be rotated by turning a magnetic rotary feedthrough (see Figure 1). In this manner, the sample could be easily aligned in the light beam.

FIGURE 1. Ellipsometer Sample Chamber.

*See references.

A Trub Tauber-KD3m high energy electron diffraction unit was used in the work. Its maximum operating voltage is 50 kilovolts (kv) at a maximum current of 1 milliamper (ma). The source of the electron beam was a cold cathode of chrome-nickel steel.

A Norelco x-ray diffraction unit was utilized with a goniometer attachment. A copper target tube was operated at 50 kv and 40 ma.

B. PROCEDURE – The experimental procedures involved in sample pretreatment and ellipsometer measurements were identical with those reported earlier (2).

1. Sample Preparation.

The samples used for ellipsometer studies were lapped to a 7- or 8-microinch surface finish, and the samples used for diffraction analysis were sanded with 250-grit sandpaper. A sample for ellipsometer measurements and one for diffraction analysis were polished with diamond abrasive (Grades 3 and 1), immediately before they were placed in the vacuum system. The sample chamber was evacuated and baked at 250°C for about 8 hours. After cooling, the pressure in the chamber was in the low 10^{-7} torr range and a "clean" surface was produced by argon-ion bombardment in 45 microns argon at 2000 volts (v) and 5 ma/in² until no further change in ellipsometer readings occurred.

Preparation of an oxide film was begun immediately after the pretreatment. The samples were heated to a preselected temperature and then 50 microns of pure oxygen were introduced into the test chamber. The desired oxide was formed either by exposure of the sample to oxygen (thermal oxide) or by oxygen-ion bombardment. Both oxides were prepared at temperatures of 50° and 100°C. Ellipsometer measurements were made as a function of time during the preparation of the oxide films. Ellipsometer data were processed using an IBM-360 computer (3).

The method used for oxidation by ion bombardment was as follows: After preparation of a "clean" uranium surface by argon-ion bombardment, the sample was maintained at a constant selected temperature by heating the entire sample chamber. Then 50 microns of oxygen were admitted. Oxygen-ion bombardment could then be carried out by applying a

negative potential of 1000 v to the sample relative to the sample chamber. A current density of 5 ma/in² resulted from these applied conditions. The oxygen-ion bombardment was performed intermittently. The negative potential on the sample was turned off at intervals to allow the sample to cool and remain at the selected oxidation temperatures of 50° and 100°C. After each bombarding interval, ellipsometer measurements were made.

In addition to a thermal oxidation caused by maintaining the sample at a constant 50° or 100°C, the oxygen-ion bombardment could produce an enhanced sticking probability and/or disturbance of the surface oxide structure.

In each experimental run, two samples were placed in the chamber. One sample was used for ellipsometer observations, and the other for HEED and x-ray diffraction examinations. No ellipsometer measurements were made on the sample for HEED analysis, and it was assumed that the oxide characteristics were approximately the same. The surface preparation for the two samples was similar, except the sample for HEED analysis had been sanded with 250-grit sandpaper before polishing to create a rough surface beneficial for the HEED patterns. After these samples were prepared in the ellipsometer chamber, the sample for HEED analysis was exposed to atmosphere and taken to the HEED apparatus where diffraction patterns were taken within a few hours. X-ray diffraction patterns were taken on this same coupon within 8 hours after HEED analysis. Previous ellipsometer measurements and HEED patterns indicated the oxide structure and thickness should not be appreciably affected by exposure to atmosphere at ambient temperature until after several days.

2. HEED Analysis.

The HEED studies were conducted at 35 to 40 kv, (0.8 – 1.0 ma), at a pressure of about 10^{-4} torr. The sample coupons used were about $\frac{3}{4}$ by $\frac{1}{4}$ by $\frac{1}{16}$ inches and were examined by the reflection technique (Figure 2). A standard diffraction pattern of magnesium oxide, deposited on an aluminum coupon, was exposed on one half of the film plate for standardization. On the other half, the diffraction pattern of the uranium coupon was exposed at the same accelerating voltage (Figure 3). The standard was necessary to determine the wavelength of the incident electrons. The wavelength

is dependent on the accelerating voltage which could not be measured with sufficient accuracy. Utilizing the known interplanar "d" spacings of magnesium oxide (4), the wavelength of the electrons was calculated as shown below:

From Figure 2,

$$\frac{r}{L} = \tan 2\theta \quad (1)$$

From Bragg's equation:

$$\frac{\lambda}{d} = 2 \sin \theta \quad (2)$$

For small values of θ , $\tan 2\theta \approx 2 \sin \theta$, therefore

$$\frac{r}{L} \approx \frac{\lambda}{d} \quad (3)$$

FIGURE 2. High Energy Electron Diffraction by the Reflection Technique. (E-Electron Beam; S-Sample; F-Film Plate; L-Sample to Film Plate Distance; and r-Distance from point where undeflected beam would strike the film to the diffraction rings.)

FIGURE 3. HEED Pattern with a Standard Magnesium Oxide Pattern on the Top Half and a Uranium Dioxide Pattern Below.

Such an approximation may be justified since the error introduced by assuming equality is smaller than the uncertainty in the measurements of r . Knowing λ , the interplanar distance "d" for the unknown uranium sample can be calculated from Equation 3.

RESULTS AND DISCUSSION

As described more completely in a previous paper (2), curves of Δ versus ψ are used to determine the indices of refraction and thicknesses of thin films. The quantity Δ is the phase difference between the parallel and perpendicular components to the plane of incidence of the reflected, elliptically polarized light. Whereas ψ refers to the angle whose tangent is the ratio of the amplitudes of the parallel and perpendicular components of the reflected, elliptically polarized light.

Ellipsometer measurements of the metal surface during the growth of the oxide films were used to establish curves of Δ versus ψ . The shape of the Δ versus ψ curves is indicative of the index of refraction of the film. The Δ versus ψ curves for the 100°C oxides as shown in Figure 4 suggest that there is an optical difference between the thermal and ion-bombardment

FIGURE 4. Experimental Δ Versus ψ Curves for Uranium Oxidation by Thermal and Ion-Bombardment Reactions in 50 Microns of Oxygen at 100°C. [Delta (Δ) is the phase difference between the parallel and perpendicular components to the plane of incidence of the reflected polarized light, and psi (ψ) is the angle whose tangent is the ratio of the amplitudes of the parallel and perpendicular components of reflected polarized light.]

oxides. The possibility exists because the two curves have an increasing divergence as the oxide thickness increases, indicating a difference in the complex index of refraction.

By matching the experimental curves with theoretical curves calculated with a specific index of refraction for the film over a thickness range, the index of refraction for the films can be determined. In this way, the indices of refraction of the thermal and ion-bombardment oxides were determined to be $(2.5 - 0.5i)$ and $(2.5 - 0.4i)$, respectively. The imaginary (i) part of the index of refraction is the extinction coefficient k , shown as 0.5 and 0.4 in the above notations. One physical significance of k is that the intensity of the light becomes attenuated in the oxide medium by a factor-- $\exp(-2\omega kx/c)$, where x is the distance traveled into the medium, ω is the angular frequency, and c is the speed of light in vacuum (5).

The lengths of the experimental Δ versus ψ curves for the 50°C oxides, thermal and ion bombardment, were not as long as for the 100°C oxides due to the slower oxide-thickness growth rate at the lower temperature. Consequently, there was more ambiguity in fitting theoretical curves to the 50°C curves. Each oxide appeared, however, to coincide with its respective 100°C curve. Therefore, the thermal and ion-bombardment oxides were assumed to have the same respective refractive indices as the 100°C oxides, i.e., $(2.5 - 0.5i)$ and $(2.5 - 0.4i)$.

Each oxidation condition was repeated to verify the shapes of the Δ versus ψ curves, and thus the differences in the extinction coefficients for the thermal and ion-bombardment oxides. Such differences were confirmed. The quantitative accuracy for the extinction coefficients was difficult to establish; however, there is a definite qualitative difference with the thermal oxide having a greater extinction coefficient than the ion-bombardment oxide.

Figure 5 shows the growth characteristics for the thermal and ion-bombardment oxidation at 50° and 100°C in 50 microns of oxygen. Oxide thicknesses were determined from the experimental Δ versus ψ curves using Winterbottom's graphical technique (2). The oxygen-ion bombardment oxidation was performed in segments with cooling intervals to maintain the sample at the preselected oxidation temperatures of 50° and 100°C. The numbers in the oxygen-ion bombardment curves indicate total time in minutes the sample was actually oxygen-bombarded.

Uranium dioxide (UO_2) was the only oxide phase identified by either x-ray or HEED. In every case, the overlaying oxide thickness was too great for the electron beam of the HEED apparatus to show diffraction patterns of the substrate metal. In the HEED and x-ray diffraction patterns, a difference was noted between the thermal and oxygen-ion bombardment oxides. The HEED patterns for the thermal oxides were rather weak and diffuse with little difference between the 50° and 100°C oxides. The ion-bombardment oxides for 50° and 100°C produced no detectable HEED patterns initially. After the bombardment oxides were exposed to air however, for a period of several days, faint uranium-dioxide patterns were observed. Similarly for x-ray diffraction, the patterns were those of uranium dioxide for both oxide types, but the patterns for the

FIGURE 5. Thickness Versus Time for Each Type of Oxidation at 50° and 100°C. (Numbers on curves indicate actual total bombardment time in minutes.)

ion-bombardment samples were broader and less intense than the thermal-oxide patterns.

Apparently, from the HEED and x-ray diffraction observations, the thermal oxides have a greater degree of crystallinity or lattice order than the oxygen-ion bombardment oxides. This is particularly evident for the surface layers as examined by HEED. The conclusion reached indicates that a structural difference between the two types of oxides is responsible for the difference in optical properties described earlier.

The two independent measurements, ellipsometry and diffraction, have shown that the ion-bombardment oxides with a lower extinction coefficient have an amorphous or less ordered structure than the more crystalline thermal oxides. It is not possible at this time to say the bombardment oxide is amorphous. The absence of diffraction lines for the HEED patterns and the broad diffuse lines for the x-ray diffraction patterns for the ion-bombardment oxides may suggest that the elevated temperature during the

bombardment may crystallize the inner layers, while the bombarding oxygen ions keep the surface layers amorphous. It appears that oxygen ions bombarding the existing oxide produce at least a surface oxide that is amorphous as judged by HEED.

SUMMARY AND CONCLUSIONS

The characteristics of uranium dioxide (UO_2) prepared by thermal and oxygen-ion bombardment techniques were determined by ellipsometry, HEED, and x-ray diffraction. A difference between the optical constants of thermally-produced and ion bombardment-produced oxides was found using the ellipsometer. The index of refraction at 5461Å of the thermal oxide is $(2.5 - 0.5i)$ and the ion-bombardment oxide is $(2.5 - 0.4i)$. HEED and x-ray diffraction analysis showed that the thermal oxides have a greater degree of crystallinity than the ion-bombardment oxides. Oxide thickness as a function of time was observed for each oxide-preparation condition, and the initial oxidation rate during oxygen-ion bombardment was found to be greater than the thermal-oxidation rate.

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