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Relative lability of gold-oxide thin films in contact with air, solvents, or electrolyte solutions

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The lability of gold-oxide thin films in contact with air, pure solvents, or electrolyte solutions was investigated by monitoring film thicknesses using spectroscopic ellipsometry. Surface compositions were monitored using low-energy ion scattering. The oxide was inert in air over 24 h, but decomposed partially in tetrahydrofuran (THF) and water, and completely in ethanol, within the same period. The film thicknesses decreased significantly in THF solutions of Bu_4NPF_6 and Bu_4NBF_4 , but were more inert in solutions of Bu_4NClO_4 and LiClO_4 in the same solvent, making the latter more suitable choices as supporting electrolytes in electrochemical studies. © 2013 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4791687>]

I. INTRODUCTION

Gold oxides are thermodynamically unstable,¹ with the exemplar Au_2O_3 having a significantly positive standard free energy of formation (78.70 kJ/mol).² As a result, gold oxides are powerful oxidizing agents, potentially important in the conversion of CO to CO_2 on gold/metal-oxide catalysts^{3–5} and even capable of carbonizing organic polymers.⁶ Nonetheless, oxide films on gold can be sufficiently inert under ordinary laboratory conditions to allow spectroscopic characterization and use in certain applications. Thin oxide films can easily be produced on gold electrochemically,^{7–10} via chemical oxidation,^{11,12} and by photochemical oxidation with O_3 .^{13,14} In addition to their use as masking films on gold electrodes to allow selective surface chemistry,¹⁵ oxide films have also proven useful as model systems for the study of interfacial phenomena such as corrosion and catalysis.^{3–5,16}

The inherent instability of gold oxide has sometimes led to cautious approaches to its study and use in order to avoid uncertainty regarding the composition of samples due to spontaneous decomposition. For example, some studies on electrochemically formed oxides have been performed under an applied anodic potential.^{17,18} Others, however, have estimated a substantial activation energy for thermal decomposition of the oxide. Temperature-programmed desorption (TPD) spectra, for example, indicated an activation energy for the desorption of O_2 from oxide monolayers on Au(111) of 30 kcal/mol (126 kJ/mol).¹⁹ Measurements of surface resistance on thicker films ($>40 \text{ \AA}$) gave a lower activation energy for the decomposition of Au_2O_3 (57 kJ/mol) and a half-life at 22 °C of 22 h.²⁰ This difference may reflect nonlinearity in the relationship between surface resistance and composition or reduction of the film by primary and secondary electrons generated by exposure to x rays during analysis by x-ray photoelectron spectroscopy in the latter study.²¹ In addition, recent examples of supported gold-oxide nanoparticles suggest that this inertness extends to the submicron size regime.^{22–25}

We recently showed that thin films of gold oxide can be used as passivation layers to allow selective reactivity on a particular gold electrode in the presence of another.¹⁵ We also developed an analytical approach, combining x-ray photoelectron spectroscopy and spectroscopic ellipsometry to determine the complex refractive index of gold-oxide thin films.²⁶ We were prompted by these studies to examine the relative lability of these films in contact with air and with various condensed phases in order to determine under what conditions they would remain intact. Although isolated pieces of data were available in the literature—e.g., its behavior in vacuum,¹⁹ air,^{20,27} and a few aqueous solutions,²⁷ and its fast decomposition (reduction) in ethanol¹⁴—this paper provides kinetics data under a range of conditions and provides a practical guide for those interested in the handling and use of this material. Of particular interest is the behavior in solutions of common electrolytes used in electrochemical studies and applications.

II. EXPERIMENT

A. General

Silver nitrate (99.8%) and tetrabutylammonium perchlorate (Bu_4NClO_4 , 99.9995%) were used as received from Fisher Scientific. Ethanol (Anhydrous, J.T. Baker, 95%) was used as received. Tetrahydrofuran (THF, Mallinckrodt, 99%) was purified and dried using a Pure Solv system (Innovative Technology). Hydrogen peroxide (30%) and sulfuric acid (95%) were used as received from EMD. Gold (99.999%) was used as supplied by VEM Vacuum Engineering. Lithium perchlorate (LiClO_4 , anhydrous, Alfa-Aesar, 99%), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4 , TCI, 98%), and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , Adrich, 98%) were used as received. Water was purified with a Millipore Simplicity[®] UV system (18.1 M Ω cm).

B. Electrochemical formation of gold oxide

Gold electrodes were prepared on $\sim 1 \times 2 \text{ cm}^2$ glass slides that had been cleaned using piranha solution. Caution: Piranha solution, a 4:1 (v/v) mixture of concentrated H_2SO_4 and

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30% H_2O_2 , reacts violently with organic material and should be handled carefully. Approximately, 150 Å of Ti (as an adhesion promoter) and then 1500 Å of Au were deposited at a rate of ~ 3.4 Å/s onto the substrates by e-beam evaporation. Prior to use in experiments, gold electrodes were cleaned by cycling their potential seven times from -0.9 to 1.2 V in 0.5 M aqueous sulfuric acid.

A thin film of gold oxide was produced electrochemically in 0.5 M aqueous sulfuric acid using a standard three-electrode cell comprising a gold working electrode, a platinum wire as the counterelectrode, and an aqueous Ag/AgNO_3 (10 mM) reference electrode. To oxidize each electrode, its potential was held at -0.2 V for 10 s, followed by 1.2 V for 10 s. The sample was then rinsed with deionized water (18.1 M Ω cm) and dried under a stream of N_2 .

C. Variable angle spectroscopic ellipsometry

Ellipsometric parameters, Ψ and Δ , were measured using a J.A. Woollam V-VASE variable angle spectroscopic ellipsometer. Data were collected at a single spot on each sample between 350 and 800 nm at 50 -nm intervals with angles of incidence of 60° and 70° . Film thicknesses were determined by fitting these parameters to an optical model using WVASE32[®] analysis software. The model consisted of a gold substrate of optically infinite thickness coated with a thin film of gold oxide of undetermined thickness and having values of n and k determined previously.²⁶ The software solves for a consistent thickness of gold oxide corresponding to the measured values of Ψ and Δ for each sample. The optical constants of our bare gold electrodes were determined after electrochemical cleaning, and prior to their oxidation.

D. Low-energy ion scattering

Spectra of samples that had been exposed to air or solutions of interest were generated using an ION-TOF Qtac 100 instrument. An iridium filament was used to produce a beam of He^+ ions with 3000 eV of kinetic energy. The ion beam struck the surface of the sample at normal incidence, and scattered ions were collected at an angle of 55° . The energies of the scattered ions were measured using an azimuthal detector operating with a pass energy of 3000 eV. Samples were analyzed under an ion current of 1.22×10^{-2} μA , with the beam rastered over a square region 2000 μm across, to give a total ion dose of 1.88×10^{14} cm^{-2} for a single scan.

Each scan sputters away a fraction of the atoms at the surface, so initially, contaminants adsorbed from the air are removed to reveal the underlying material of interest. Surface contamination or overlayers (e.g., oxides) can lead to more efficient reionization of scattered He atoms that were neutralized during inelastic collisions with the sample. These ions appear as a “tail” of intensity on the lower-energy side of peaks due to elastic, binary collisions. As such, the intensity of this tail can be used as a qualitative measure of the amount of contamination or oxide on the sample surface. We therefore monitored the intensity of the low-energy tail after successive scans until the change from scan to scan was (qualitatively) small and peaks due to elastic binary collisions with the ion

beam were observed. At this point, we considered the last scan to best represent the composition of the uncontaminated surface. To minimize the removal of any oxide during this process, we also monitored the region of the spectrum (~ 1140 eV) where ions scattered elastically from single collisions with oxygen on the surface would be expected. The eighth scan is reported for the samples aged either in air or in a solution containing tetrafluoroborate ion, whereas the fifth scan is reported for the sample exposed to a solution containing hexafluorophosphate ion.

III. RESULTS AND DISCUSSION

Gold electrodes were oxidized electrochemically at 1.2 V (vs 10 mM AgNO_3/Ag) in 0.5 M aqueous sulfuric acid to produce thin oxide films having an average ellipsometric thickness of 9 ± 1 Å.^{7–10,26} The presence of an oxide was confirmed by the appearance of a large cathodic wave in a linear sweep of potential in 0.5 M sulfuric acid, corresponding to reduction of the oxide to the metal (Fig. 1). As also shown in Fig. 1, this peak is absent from a scan of unoxidized gold. The thickness of the oxide films was monitored as a function of the amount of time the film was in contact with the ambient atmosphere, a solvent, or an electrolyte solution. Initial measurements of the oxide thickness within 5 min of their formation are treated as occurring at $t = 0$ in plots of the data. Representative plots of the ellipsometric parameters, Ψ and Δ , for gold and gold oxide—used to calculate film thickness—are shown in Fig. 2. These data are close to those reported previously for Au_2O_3 films formed by UV/ozone treatment of gold.²⁷ After the initial film thickness was measured, each sample was placed into a separate 20 -mL scintillation vial containing air or a test liquid. The film thicknesses were monitored by collecting ellipsometric data after removing the sample and rinsing with THF and deionized water (THF solutions), or with just deionized water (for the water-soaked sample), and drying under a stream of N_2 . After each measurement, the samples were placed back into their respective vials. Data were collected at 15 -min intervals over the course of an hour, followed by a final measurement collected after 24 h. These choices reflect the timescale of typical electrochemical experiments. Each experiment was

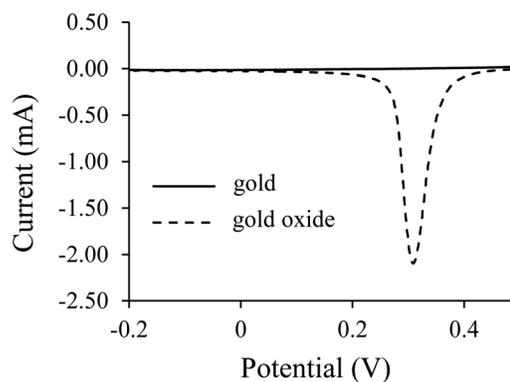


Fig. 1. Cathodic linear potential sweep (0.1 V/s) in 0.5 M sulfuric acid of a clean gold electrode (solid line), and an electrochemically oxidized gold electrode (dotted line).

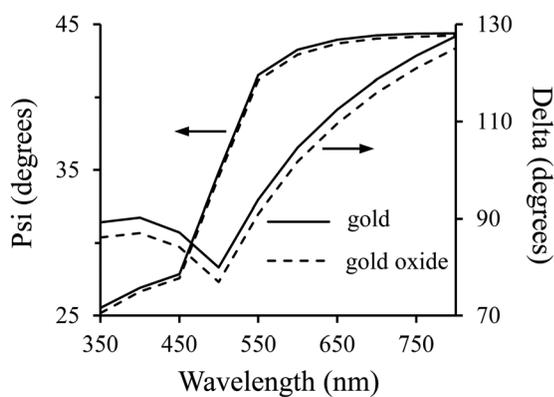


FIG. 2. Measured ellipsometric parameters, Ψ and Δ , plotted as a function of wavelength for gold (solid line) and electrochemically formed gold oxide (dotted line) in air. These data were collected at an angle of incidence of 70° .

repeated in triplicate, and data are reported as the average of each set of measurements.

A. Lability in air and solvents

Figure 3 shows the thickness of oxide films on gold electrodes in contact with air, THF, deionized water, or ethanol. In air, the thickness remained unchanged over the entire 24-h period, which is more consistent with the large activation energy reported from TPD studies¹⁹ than that based on measurements of surface resistance.²⁰ A low-energy ion scattering (LEIS) spectrum of a sample taken after 1 h of exposure to air confirmed the presence of the oxide layer, revealing peaks due to elastic, binary collisions with both gold and oxygen (Fig. 4). The large reionization tail on the lower-energy side of the Au peak is consistent with the presence of a thin oxide overlayer at the surface of the sample.²⁸

In THF, the film thickness was constant during the first hour of immersion, but decreased by about 33% over the

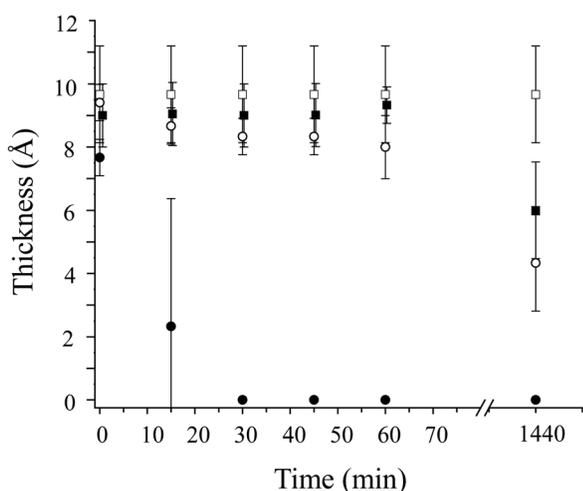


FIG. 3. Ellipsometric thickness of gold-oxide thin films in air (open square), THF (filled square), water (open circle), and ethanol (filled circle) as a function of time. The values reported are the average of three measurements, and the error bars represent the standard deviation of these measurements. All data were taken at 15-min time intervals; overlapping points have been shifted slightly in the horizontal direction for clarity.

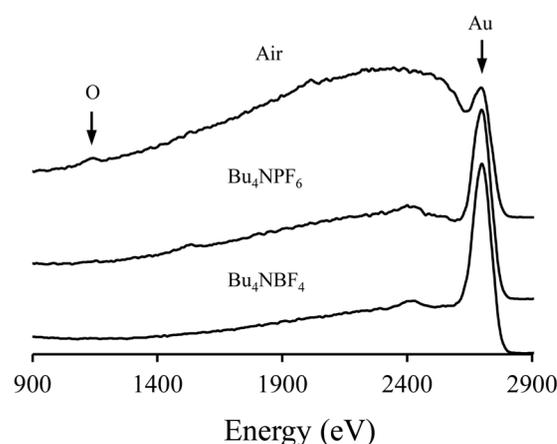


FIG. 4. Low-energy ion scattering spectra from thin films of gold oxide that had been exposed to air, or solutions of Bu_4NPF_6 or Bu_4NBF_4 in THF for 1 h.

next 23 h. Samples immersed in water behaved similarly, though decomposition occurred at a somewhat faster rate: their thickness decreased slightly during the first hour, but degraded by $\sim 50\%$ over the next 23 h. This behavior is consistent with, but does not demand, the presence of a mixed oxide (e.g., compact and hydrous oxide, α and β , respectively)^{10,29,30} having components of differing solubility in water or THF that contains water adsorbed from the ambient atmosphere. Gold (III) hydroxide, for example, is reported to be soluble in water by formation of complex ions.^{31,32} The data in Fig. 3 also show that ethanol is a sufficiently strong reducing agent to quickly reduce oxide films on gold, consistent with previous reports.^{14,15} In this case, the oxide was completely removed within the first 30 min of immersion. Atomic force microscopy indicated little or no change in surface morphology between an electrode surface prior to oxidation and after oxidation and reduction in ethanol.³³

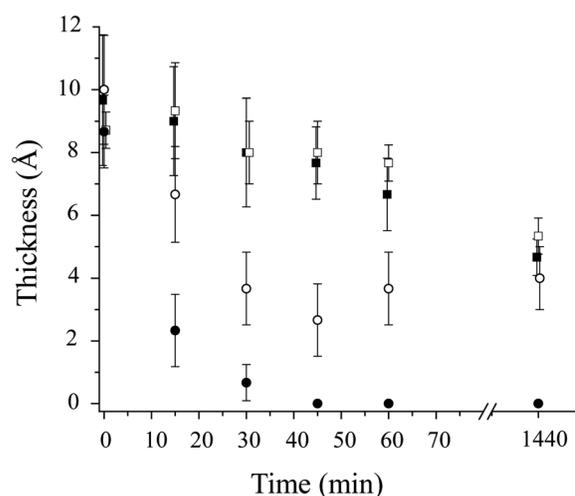


FIG. 5. Ellipsometric thickness of gold-oxide thin films in THF solutions of Bu_4NClO_4 (open square), LiClO_4 (filled square), Bu_4NPF_6 (open circle), and Bu_4NBF_4 (filled circle) as a function of time. The values reported are the average of three measurements, and the error bars represent the standard deviation of these measurements. All data were taken at 15-min time intervals; overlapping points have been shifted slightly in the horizontal direction for clarity.

B. Lability in electrolyte solutions

To examine the behavior of gold oxide under conditions relevant to electrochemical applications, the oxide thickness on gold electrodes was monitored in 0.1 M THF solutions of salts commonly used as supporting electrolytes in organic solvents, Bu_4NClO_4 , LiClO_4 , Bu_4NBF_4 , and Bu_4NPF_6 (Fig. 5). Consistent with the results for pure THF, films immersed in each of the electrolyte solutions tested decreased in thickness significantly over 24 h, though there were large differences in both rate and extent of decomposition. In these experiments, the oxide was most inert in solutions of the perchlorate salts, for which the film thickness gradually degraded somewhat (by 10–30%) during the first hour and ultimately lost 40–50% of their thickness over the 24-h period.

In stark contrast to the perchlorate results, the solution containing tetrafluoroborate ion caused complete loss of the oxide film within 30–45 min. This behavior was confirmed with LEIS: the spectrum of a sample immersed in a solution of tetra-*n*-butyl ammonium tetrafluoroborate for 1 h showed a large peak due to gold, and no peak due to oxygen (Fig. 4). These results, as well as the low intensity of the low-energy tail, suggest the lack of an oxide overlayer on this sample. The accelerated decomposition in this solution may reflect etching of the oxide by HF, which could be formed by hydrolysis of tetrafluoroborate ion.^{34,35} Although the THF used in these experiments was initially dry, the solutions were handled in air and thus contained small amounts of water that could lead to hydrolysis.

For comparison, the behavior of samples in solutions containing hexafluorophosphate ion was intermediate between those in solutions of perchlorate and tetrafluoroborate salts. Their thickness fell by more than 50% during the first 30–45 min, but remained relatively constant thereafter. As shown in Fig. 4, a sample immersed a solution of tetra-*n*-butyl ammonium hexafluorophosphate ion solution for 1 h and analyzed by LEIS indicated a much-diminished oxide layer. The spectrum contained a prominent peak due to gold and only a hint of oxygen. The larger intensity of the low-energy tail, relative to that of the sample exposed to tetrafluoroborate ion, is consistent with the presence of at least a partial oxide layer at the surface. The slower decomposition in the presence of PF_6^- , relative to BF_4^- , is consistent with the lower susceptibility of the former to hydrolysis. The equilibrium constant for hydrolysis of PF_6^- in water, for example, is 1.5×10^{-15} at 25 °C, and that of BF_4^- is 2.7×10^{-3} at 30 °C.^{36,37} To the extent that this difference in reactivity may be reflected in wet THF, it could influence the concentration of HF available to etch the oxide.

IV. SUMMARY AND CONCLUSIONS

In summary, the lability of gold-oxide thin films varies significantly in different environments. The thickness of these films remains unchanged in air for at least 24 h, though significant decomposition occurred over the same period upon immersion in pure solvents, water or THF. In ethanol, a mild reducing agent, the oxide was quickly reduced to the metal. The behavior in electrolyte solutions depended strongly on

the anion of the electrolyte. Fluorine-containing ions had the strongest effect on film thickness. Solutions of Bu_4NPF_6 in THF caused a significant decrease of the oxide film thickness in less than an hour, and solutions of Bu_4NBF_4 caused complete decomposition within 45 min. The action of these solutions, as well as the difference between them, may reflect the susceptibility of the anions to hydrolysis to produce HF. Oxide films were more inert in solutions of Bu_4NClO_4 or LiClO_4 in THF, making these electrolytes better candidates for short-term electrochemical experiments involving gold oxide.

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- ¹Although the term “thermodynamically (un)stable” is redundant, we nonetheless use it, and related constructions, to provide as sharp a distinction as possible between the thermodynamic terms, stable and unstable, and the kinetic terms, inert and labile.
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