NATIONAL BUREAU OF STANDARDS REPORT

9802

SILVER OXIDATION IN ATOMIC OXYGEN

for

The Goddard Space Flight Center
of the
National Aeronautics and Space Administration
Contract S–998142–G

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

[2] Located at Boulder, Colorado, 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT
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SILVER OXIDATION IN ATOMIC OXYGEN

by

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and
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for

The Goddard Space Flight Center
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Final Report on NBS Project No. 3120444

U.S. DEPARTMENT OF COMMERCE

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The work reported here is concerned with problems which arose in measuring the amount of atomic oxygen in the earth's upper atmosphere by the Goddard Space Flight Center of the National Aeronautics and Space Administration. Preoxidized silver has been proposed as a surface coating on stainless steel for the gas entrance chambers of a satellite mass spectrometer for measurement of the earth's upper atmosphere components. It was speculated that silver, which had been preoxidized with atomic oxygen would behave as a catalytic surface for the recombination of atomic oxygen from the environment. After this recombination the oxygen would not undergo any further trapping reactions before measurement in the spectrometer. The question that this work answered was whether or not a stable surface can be formed prior to use in the measurement process so that no further oxide formation or film growth would introduce uncertainties into the measurement of the atomic oxygen in the upper atmosphere. Also of interest was the stability of the surface formed under the low pressures associated with the altitudes of measurement.

The specimen used for the study at the NBS was a 99.999% pure, bulk, polycrystalline sample (see Table I for analysis). The specimen was placed in a cell designed for incorporation into a high vacuum system for the *in situ* ellipsometric study of metal surfaces exposed to atomic oxygen. Film growth to thicknesses of up to about 5000 Å

could be measured with the ellipsometer for the particular film and substrate under investigation. The technique of ellipsometry[1,2] determines thickness and optical constants of films on metal surfaces by measuring the change in state of polarization of a light beam upon reflection. The specimen was mechanically polished ending with a 6 micron diamond abrasive. An etching solution of about 50% reagent HNO_3 was used after each stage in the polishing. Electropolishing was then accomplished in a cyanide bath containing the following proportions of constituents: 35g AgCN, 37g KCN, 38g K_2CO_3 to 100 ml H_2O. Optimum conditions for polishing were established when the voltage oscillated between about 0.8 to 1.7 volts. The specimen was given a final rinse in spectro-grade methanol and dried in a stream of pure oxygen. After positioning in the cell, the specimen was cleaned and annealed at 2×10^{-7} torr by induction heating to red glow (about 600°C). This was repeated until ellipsometer readings from the surface ceased to change significantly upon subsequent heatings, denoting no further oxide removal. After cooling to room temperature, atomic oxygen, produced in a microwave discharge, was beamed to the center of the area under observation across a pressure differential through a capillary. The pressure in the vacuum system during the study was about 10^{-8} torr, although during the atomic oxygen exposure a pressure of about 10^{-1} torr on the high side of the capillary was required to maintain the discharge.

We found that the silver oxide film continues to grow under constant atomic oxygen bombardment, following a logarithmic growth rate. This indicates that the oxidation rate controlling step is a solid diffusion mechanism, and that more than enough oxygen is absorbed to continue the process. The growth appears to be two stage with a slight increase in the logarithmic rate constant after a thickness of around 2200 Å is attained (see Figure 1). In addition to ellipsometric observations it was possible to follow visually changes in thickness by means of interference colors as the thickness increased until the surface became blackened (greater than 5000 Å). The microwave discharge of O_2 is known to produce uncertain proportions of various species such as O, O^-, O^+, O_3, and exited states. For this reason, further mechanistic interpretation at the present time would be largely speculative.

Approximate optical constants found for the 5461 Å wavelength of the Hg arc light source used in this experiment were for the "clean" silver, $\hat{n} = 0.140 - 3.29i$, where $\hat{n} = n(1-ik)$; n = real refractive index, k = absorption coefficient. Optical constants of the oxide were determined by a method of best fit to computer calculated curves. The ellipsometer computer program produces tables of polarizer and analyzer values for a range of thicknesses corresponding to given values of optical constants of the film and substrate. Constants of the substrate being known, values for the oxide were found by matching the experimental readings with those of the computer tables to find the best correspondence.

These values were found to be $\hat{n} = 2.00 - 0.085i$.

After the silver oxide film had been formed and the atomic oxygen bombardment stopped, its thickness decreased a small amount as the gas was pumped out of the system. Upon restarting the atomic oxygen beam, the film was found to regrow at the same rate as before. Investigators at NASA[3] found that an oxidized silver surface grown in a similar manner consisted of approximately 30% AgO and 70% Ag_2O which upon heating to about 150°C in vacuum was converted to 100% Ag_2O. At low pressures and room temperature, the stable oxide is probably nearly all Ag_2O. Since the dissociation of AgO at the pressures existing in the evacuated system is favored thermodynamically, the instability in the oxide film seen on removal of oxygen after oxidation, is explicable.

Since it was found that film growth never stops when silver is exposed to atomic oxygen, it must be concluded that the pre-oxidized silver surface is not suitable for making measurements of the concentration of atomic oxygen by using it for the catalytic recombination of the oxygen atoms to be measured as molecular oxygen. These results indicate that some of the atomic oxygen remains on the surface as part of the oxide film. Additional silver oxidation investigations are being continued and funded by the National Bureau of Standards.

REFERENCES

1. McCrackin, F.L., Passaglia, E., Stromberg, R.R., and Steinberg, H.L., "Measurement of the Thickness and Refractive Index of Very Thin Films and the Optical Properties of Surfaces by Ellipsometry", J. Res., NBS, Vol. 67A, No. 4, 363 (1963).

2. Ellipsometry in the Measurement of Surfaces and Thin Films, Symposium Proceedings, National Bureau of Standards Misc. Pub. 256, E. Passaglia, R.R. Stromberg and J. Kruger, editors, U.S. Gov't. Printing Office, Washington, D.C. (1964).

3. Private communication.

TABLE I

Spectrographic Analysis of 99.999 + % Silver

Element	PPM
Mg	2
Si	<1
Fe	<1
Cu	2

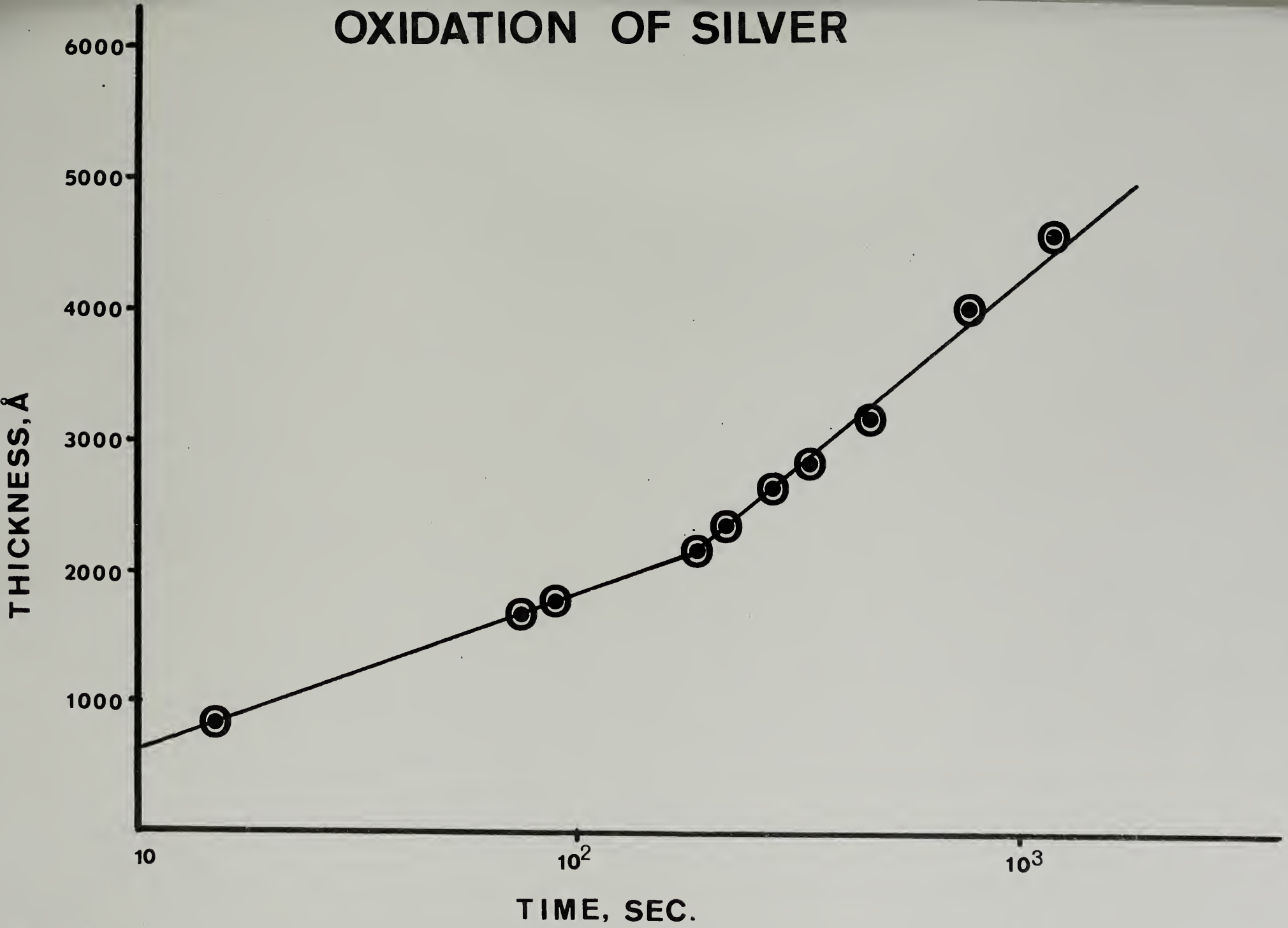
OXIDATION OF SILVER
6000
5000
4000
3000
2000
1000
THICKNESS, Å
10
10^2
10^3
TIME, SEC.

FIG.1


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