

MEASUREMENTS OF THE OPTICAL PROPERTIES
OF THIN FILMS OF SILVER AND SILVER OXIDE

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SUMMARY

The optical properties of silver films and their oxides are measured to better characterize such films for use as sensors for atomic oxygen. Good agreement between properties of measured pure silver films and reported optical constants is observed. Similar comparisons for silver oxide have not been possible because of a lack of reported optical constants, but self-consistencies and discrepancies in our measured results are described.

INTRODUCTION

Silver, because of its electrical and optical properties, has many uses; however, silver's tendency to tarnish limits its optical film applications, and its susceptibility to destruction by atomic oxygen in low Earth orbits severely limits its applications in space.¹⁻⁴ Such changes in properties, however, have been used as sensors of atomic oxygen.⁵⁻⁸ While silver films are inexpensive and relatively simple sensors compared to mass spectrometers, or other complicated instruments, they exhibit some complexities that affect interpretation of exposure results. Optical measurements, such as reflectance and transmittance of silver films, are also relatively simple to do, but to accurately quantify oxygen atom exposure it is necessary to know the optical constants of the materials and to be able to model the material distributions. The studies reported here were performed to help measure such constants and to develop models, which are presently lacking.

One difficulty that arises is that silver is not useful for very heavy exposures. While measured effects have been found to be fairly linear over a specified range, excessive exposure leads to nonlinearity, cracking, debonding, and loss of the oxide's specular appearance.^{3,9} Using silver films of limited thickness can solve the above problems, if the possibility of saturation is recognized. Another problem can arise when the silver films are too thin; below approximately 25 nm thickness silver films have been found to exhibit an increase in extinction coefficient k and a decrease in the index of refraction n , with k peaking between 10 and 20 nm, and the absorption was dependent upon deposition rates.¹⁰ Such films were found to be discontinuous and treated as incompletely coagulated particles. The formation of both

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oxides of silver, AgO and Ag₂O, causes a large expansion of the silver lattice,^{2,3} which, for excessively thick films, causes the debonding and loss of specular characteristic. The resulting brown-gray or black-gray oxides fit the descriptions given for them in handbooks.¹¹ However, for thinner, specular oxide films the properties are more characteristic of coated optics.

The high reflectance and strong absorption of light by pure silver results in a rapid loss of intensity and minor interference between wavefronts reflected from top and bottom interfaces of a silver film; approximate linearity of optical density with thickness results and a simple Beer's Law model is reasonably appropriate, where $I=I_0e^{-at}$ is used to determine the transmittance; however, the greater transparency of silver oxide causes obvious interference effects, which cannot be neglected in interpretation of the measurements. Determination of a suitable model and optical constants to describe measured results on the partially oxidized films has not been easy for a number of reasons. For silver films initially thin enough to be transparent, a strong effect of exposure to oxygen atoms is an increase in light transmittance as the pure silver is thinned by oxidation. The kinetics of this oxidation process are still being investigated, and there are difficulties with determining the exact distributions of oxide and unreacted silver as a function of depth, because attempts to measure such distributions can tend to decompose the relatively unstable oxides. A simplified model of a layer of pure oxide on pure silver on glass, although tentative, is much easier to treat theoretically and has some merit, as will be discussed. Interference effects associated with the silver oxide films can exhibit colors which are dependent upon the oxide thickness, much like oil on water or antireflection films on optics. These effects produce maxima and minima in the reflectance and transmittance versus wavelength or film thickness plots. We have previously noted that not being able to properly correct for interference effects was a potential problem in previous studies.⁷

In summary, we have relied upon optical changes to measure the effects of atomic oxygen exposure for a number of applications, and appropriate optical constants are needed for calculations in the modeling. Due to a lack of published optical constants for silver oxide, we have embarked upon extracting such constants from silver films prepared in the same manner as films we have used; these films are oxidized at ambient temperature with a thermal oxygen, rf-discharge source, and thickness, reflectance and transmittance measurements are made. Subsequent studies will consider effects of source and exposure parameters.

EXPERIMENTAL

Following prolonged pumpdown and approximately 30 minutes presputtering, silver films were deposited on Corning 7059 glass substrates using rf sputtering from a 6 inch diameter silver target with argon at 4 microns pressure and using 200 watts forward power; similar conditions previously produced niobium films with the order of one-percent oxygen, probably associated with the low residual water peak observed in the residual gas just before the presputtering was used to getter the system. Silver is probably a poorer getter than niobium, but its sputter yield, and thus deposition rate, are several times higher; relatively low oxygen content might also be expected in the deposited silver films, although contamination levels have not been accurately measured; however, reasonable agreement with published optical properties have been observed.

Film thicknesses were initially estimated by the time of deposition and accurately measured by stylus profilometry traces across fine scratches produced in the silver to expose the substrate; a technique previously reported.^{3,12} Diffuse transmission measurements were made using four relatively broadband filters centered around yellow, green, blue, and red wavelengths in a densitometer having a 1 mm diameter source aperture. Both optical density and transmittance were determined.

Reflectances were measured from 250 nm to 2500 nm with the source beam incident at 15° off-normal to the sample, which covered a 12.5 mm diameter hole in an integrating sphere (AZ Technology LPSR-200 instrument). Comparisons were made to several standards to assure calibration within instrument specs.

MODELING

The films were treated as one or more layers, each of homogeneous material, on a Corning 7059 glass substrate. The initial silver film was treated as one layer on the substrate, and any oxide was treated as a second uniform film of given thickness on top of the silver. This simplified model ignores the possibility of the oxide density decreasing with distance from the top surface, but there appears to be some support for the uniform layering in the results observed.

Measurements on most intermediate thickness films exhibit a consistent ratio between the thickness of a silver oxide film and its initial silver thickness; this agrees with published density changes being accommodated by an appropriate increase in thickness of about 58%. Large deviations from this 58% expansion and anomalies in the optical constants when the films are on the order of 10 nm thickness indicate that a separate model is needed for the thinnest films. This may be accounted for by several factors: the films may consist of aggregate particles which create a lower film density, the probability is higher that thinner films might contain more contamination from the substrate as deposited, and the thinnest films may be more poorly represented by the bulk or thicker film physical and optical properties used in the calculations. Also, for films exceeding several hundred nanometers thickness debonding or surface roughening problems are more likely to appear, which would require additional modeling.

Although in many cases film properties are sensitive to deposition techniques and measured optical properties may only be applicable to films produced under the same conditions at the same facility, the properties of pure silver films from our facility seem to agree with those from other facilities; thus, the use of published optical constants for silver seems appropriate for calculations on films of intermediate thickness. While our extracted results show some self-consistency, more studies are required to clarify discrepancies, further verify the results, and to determine to what extent the constants are dependent upon exposure conditions and other parameters during formation of the oxides.

DISCUSSION

As deposited, the silver films exhibited optical properties of pure silver, as characterized by measurements of reflectance and transmittance in air and by comparison to calculated reflectance and transmittance using published optical constants. The results of these comparisons are shown in Figs. 1 through 4. Figure 1 compares the reflectance of pure silver as measured from a 168 nm film (line with open squares) with values calculated for a number of wavelengths (*); also shown in Fig.1 is the reflectance of the same film after exposure to a beam from an oxygen discharge. Figure 2 shows measured optical densities for pure silver films of different thicknesses using four different broadband filters in the densitometer. The near linear behavior approximates Beer's Law described earlier, except for very thin films. Figure 3 shows the transmittances of the same films obtained from the measured optical densities, and Fig. 4 was obtained by calculating transmittance versus film thickness using published optical constants (single wavelengths near the filter centers were used in the calculations). The published constants, which are for thicker films, are not appropriate for films below 20 nm thickness, because silver films this thin tend to be inconsistent and produce variable properties due to variations in the aggregates that form. Thus, the calculations in Fig. 4 do not show the deviations in properties observed in very thin films that are most sensitive to deposition parameters; however, peaks, as observed near 13 nm in Fig. 3, have been reported for certain deposition conditions.¹⁰ The absorption coefficient for pure silver is sufficiently large that a rapid decay in light intensity occurs with depth in the film, limiting the transmission to films about 100 nm or less in thickness and subduing any interference effects. Silver transmits the shorter wavelengths better than the other colors, with the results that white light appears more blue when viewed through the silver and the measured transmittance is greater when shorter wavelength filters are used in the densitometer, as seen in Fig. 3.

When the silver films are oxidized, the lattice expands. For continuous films approaching bulk densities, lateral motion across the surface of the substrate is restricted, which favors vertical displacement,

or increasing film thickness; volume increases due to oxidation thus cause a proportional thickness increase. Figure 5 shows the expansion on oxidation (i.e. the ratio of oxidized film thickness to original silver film thickness) versus the original silver film thickness; to obtain this data, a number of different film thicknesses of silver were completely oxidized. The films near 20 nm and below show too little thickness change compared to the theoretical 1.58 value calculated from volume changes produced by oxidizing the films. This would be observed if the silver film consisted of aggregates, rather than being continuous, and expanded in three dimensions instead of thickness alone; adjacent voids would permit the lateral swelling. This interpretation is also consistent with the optical anomalies described above for films below 20 nm in thickness.

Figure 6 shows the general increase in transmittance with exposure time in seconds; different samples of approximately 31 nm thickness were separately exposed to the beam, each for a progressively longer time to obtain the increasing oxide thickness; this was done because returning the same sample to the beam after air exposure multiple times gave poor results. Because the oxide is relatively transparent, interference effects superimposed upon a slow decay in transmittance due to absorption are to be expected, as illustrated in Fig.7, where measured transmittance is plotted versus silver oxide thickness on 7059 glass. Again, numerous samples were used, but this time each was of different initial silver film thickness before being totally oxidized. Figure 8 is a theoretically predicted version of Fig.7 for a wavelength of 550 nm, where constant values of $n=3.1$ and $k=0.2$ were associated with all oxide thicknesses. Some of the disagreement between measured and calculated results may be related to the granular structures in thin films; however, other explanations seem necessary for all the observed discrepancies; the apparent lack of peak shifts with wavelength for the measured data seems strange, but the sparse data may not be providing satisfactory locations of the peaks and dispersion would influence peak location, as mentioned later. Another uncertainty is that uniformly complete oxidation is assumed in this case, which does not allow for variations in density or other parameters due to under or over exposure or other influences.

The effects of oxygen atom exposure on silver as a function of time were simulated by exposing 10 films, each over 500 nm thick, for increasingly longer periods. These results are shown in the Table, and the measured reflectances for the 10 films vs. wavelength are shown in Fig. 10. Attempting to obtain optical constants for silver oxide at a wavelength of 550 nm by adjusting n and k to produce the reflectances measured for each of the 10 oxide thicknesses shown in Fig. 10 causes problems similar to those in trying to fit the transmittance data of Fig. 7 by the calculations in Fig. 8; no pair of n and k values appears to satisfy all of the data points, and exact causes for all of the discrepancies have not been satisfactorily analyzed yet, but film structure, homogeneity and other factors that may be influenced by exposure conditions are being considered, and the accuracies of the oxide thicknesses, which are estimates in some cases, cannot be neglected in the analysis. It should be pointed out that reflectance measurements on a silver film flown on STS-4 gave a value of n estimated to be greater than 3, and results obtained from orbital exposure are not inconsistent with some of these ground-based results. Improper application of the same constants to a wide range of wavelengths gives qualitative agreement between measurements and calculations, but the interference maxima and minima locations are shifted, when comparing such calculated curves to the measured curves; this would be expected for a material with dispersion.

We have made limited extractions of optical constants as a function of wavelength from our measurements, but recent determinations of constants for two samples have been made using an ellipsometer with variable angle of incidence and wavelength;[#] these results suggest considerably more dispersion exists than in a typical glass, especially in the visible. If such dispersion is sensitive to exposure conditions, some of the observed discrepancies may be due to this. The ellipsometry and other results will be expanded and reported in the future.

Several computer programs to calculate reflectances and transmittances were written utilizing different techniques reported in the literature.¹⁴ All programs have given the same results where their applications overlapped. Metals, dielectrics, and semiconductors are treated, but each layer is considered to have uniform isotropic properties.

The assumption of uniform properties within each layer seems arbitrary, especially when

[#]Ellipsometry measurements by Mr. John Reynolds

partially oxidized silver films are treated as layers of pure oxide over pure silver, but the results appear to agree with some features of such a model, and while nonuniformities and anisotropies in the layers may be contributing to observed discrepancies, such effects are difficult to characterize. In the model used here, the total film thickness associated with a partially oxidized film is obtained by multiplying the thickness of silver consumed by 1.58 and adding the remaining unaltered silver thickness. The uniform layering is suggested not only by comparison of optical calculations and measurements, but also by stylus profilometry traces across scratches in films which indicate a sharp plateau at depths in the films where the boundary between the oxide layers and the silver should be expected, see Fig. 9; this suggests layering with fairly sharp changes in the mechanical properties at the interface. With further confirmation and study, such a model will also enable conclusions to be drawn about the kinetics of the silver oxidation process, at least under conditions like those described above.

The 5% precision for the measurement determining the 1.6 ± 0.05 times thickness increase upon oxidation (see Fig. 5) does not permit selecting which oxide forms, AgO or Ag₂O, since only 3% difference in the results would be predicted by substituting one oxide for the other. However, x-ray diffraction (XRD) results indicate our films are predominantly Ag₂O, as shown in Fig. 11.

It should be noted that the oxidation of silver at ambient temperature by active oxygen species involves numerous parameters, all of which are not known. There appears to be a variable lag between the initiation of exposure to our oxidizing beam and the appearance of rapid oxidation. There is also a similar effect if a partially oxidized film has been exposed to air and returned for additional exposure to the beam. The lag appears to be too long to remove a monolayer of combustible contaminant, but silicone contaminants at monolayer levels or effects of water vapor on the surface might be contributors. Heavy layers of contamination seem unlikely, unless polymerization, or some other fixation process is converting vapors adsorbed in the laboratory to films not easily evaporated during pumpdown in the oxygen source chamber. The major difficulty resulting from the above variable lags in starting time for the oxidation is that the use of timing for estimating the oxidation thickness is rather inaccurate, especially if thinly oxidized films are desired.

The ratio of Ag₂O to AgO in the oxidized films may be a parameter influenced by the type of O-atom source and exposure conditions. Conversion from AgO to Ag₂O after exposure may be a factor also, since slow changes over a period of months appear to occur and are accelerated by stresses, such as exposure in a scanning electron microscope, elevated temperature, and other parameters. Further investigations of factors influencing the ratio of the two oxides in the oxidation process are needed. Any differences in optical properties that exist between the two oxides are also needed, especially if the oxide ratios change with time, with in-depth location, or are different for thick and thin films.

CONCLUSIONS

Although the properties of silver oxide are relatively complicated, it appears that, with proper precautions, inexpensive, uncomplicated hardware can be used to perform optical measurements on silver films to gage exposure to atomic oxygen. The physical and optical properties of silver films below 20 nm and above 400 nm may be unsuitable for obtaining meaningful data; even in the intermediate thickness range there are some complications associated with nonlinearity between exposure time and measured effect. While it seems feasible to deposit pure silver films reproducibly, the initial oxidation of the films may be variably delayed during exposure by contaminants from open air or from some other cause; thus, very low levels of timed exposure may not produce the expected effect. Whether in situ film deposition might solve this problem is not known. Also, the properties of intermediate thickness films, which have specular surfaces and are relatively transparent, are significantly different from the brown-gray and black-gray powders usually described in the handbooks; this is not too different from the properties of transparent oxides of iron used for photolithography masks and the opaque red, or black, oxides associated with rust or powdered iron oxide; the optical properties of silver oxide have not received appreciable investigation at this time, probably because formation of these films has not been a common practice, but much better

characterization of the optical properties of silver oxide are needed for really accurate interpretation of optical measurements. Attempts to evaporate, sputter, or even bombard the oxides with appreciable energy results in decomposition ($T=100^{\circ}\text{C}$ decomposes AgO and 280°C decomposes Ag_2O). Silver oxide's optical properties appear to be useful enough in the intermediate thickness films to justify the effort required to determine them. The results of this study give some preliminary values for such optical constants and a layer model for the oxidation. Additional studies now in progress hopefully will confirm these results using different measurements and expand and better define their range of application.

REFERENCES

1. Gregory, J.C.; and Peters, P.N.: Interaction of Atomic Oxygen with Solid Surfaces at Orbital Altitudes, *Proceedings, First LDEF Mission Working Group Meeting (NASA, Langley Research Center)*, 1981, p.48.
2. Peters, P.N.; Linton, R.C.; and Miller, E.R.: Results of Apparent Atomic Oxygen Reactions on Ag, C, and Os Exposed During the Shuttle STS-4 Orbits, *Geophysical Research Letters*, Vol.10, 1983, p.569.
3. Peters, P.N.; Gregory, J.C.; and Swann, J.T.: Effects on Optical Systems from Interactions with Oxygen Atoms in Low Earth Orbits, *Applied Optics*, Vol. 25, April 15, 1986, pp.1290-1298.
4. Whitaker, A.F.; Little, S.A.; Harwell, R.J.; Griner, D.B.; DeHaye, R.F.; and Fromhold, A.T.: Orbital Atomic Oxygen Effects on Thermal Control and Optical Materials-STS-8 Results, *AIAA-85-0416, AIAA 23rd Aerospace Sciences Meeting*, 1985.
5. Henderson, W.R.; and Schiff, M.I.: A Simple Sensor for Atomic Oxygen in the Upper Atmosphere, *Planetary Space Science*, Vol.18, 1970, p.1527.
6. Thomas, R.J.; and Baker, D.J.: Silver Film Atomic Oxygen Sensors, *Canadian Journal of Physics*, Vol.50, 1972, p.1676.
7. Gregory, J.C.; and Peters, P.N.: A Measurement of the Angular Distribution of 5 eV Atomic Oxygen Scattered off a Solid Surface in Earth Orbit, *Rarefied Gas Dynamics*, ed. by V. Boffi and C. Cercignani, B.G. Teubner Stuttgart, 1986, pp.644-656.
8. Peters, P.N.; and Gregory, J.C.: Pinhole Cameras as Sensors for Atomic Oxygen in Orbit; Applications to Attitude Determination of the LDEF, *Proceedings of LDEF First Post-retrieval Symposium*, ed. by A.S. Levine, NASACP-3134, Part 1, June 1991, pp.61-67.
9. Edwards, D.L.; Williams, J.R.; Fromhold, A.T.; Barnes, P.A.; Wey, J.P.; Neely, W.C.; and Whitaker, A.F.: The Oxidation of Polycrystalline Silver Films by Thermal, Ground-State Atomic Oxygen, *Nuclear Instruments and Methods in Physical Research*, B79, 1993, pp.676-679.
10. Heavens, O.S.: Results of Measurements on Silver Films, *Optical Properties of Thin Solid Films*, Dover, New York, 1991, pp.166, 167, and 192-194.
11. Weast, R.C., ed.: Physical Constants of Inorganic Compounds, *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio, 1971, p.B-135.
12. Christl, L.C.; Gregory, J.C.; and Peters, P.N.: Measurements of Erosion Characteristics for Metal and Polymer Surfaces Using Profilometry, *Proceedings of First LDEF Post-Retrieval Symposium*, Kissimmee, Fla., June 2-8, 1991; ed. by A.S. Levine, NASA CP-3134, pp.723-735.
13. Lynch, D.W.; and Hunter, W.R.: Optical Constants of Metals, *Handbook of Optical Constants of Solids*, ed. by E.D. Palik, Academic Press, Orlando, 1985, pp.353-357.
14. Heavens, O.S.: *Ibid.* pp.46-95.

Table : Effects of increasing the O exposure on silver films

| EXPOSURE TIME (MIN.) | UNEXPOSED FILM THICKNESS (nm) | EXPOSED FILM THICKNESS (nm) | OXIDE FILM CALCULATED THICKNESS (nm) | OXIDE FILM MEASURED THICKNESS (nm) |
|----------------------|-------------------------------|-----------------------------|--------------------------------------|------------------------------------|
| 5 | 554.8 | 567.1 | 33.5 | NA |
| 8 | 553.7 | 555.5 | 4.9 | NA |
| 10 | 544.4 | 558.0 | 37.0 | NA |
| 12 | 550.3 | 575.2 | 67.8 | NA |
| 15 | 502.7 | 555.7 | 144.3 | 136.8 |
| 17 | 540.8 | 576.5 | 97.2 | NA |
| 20 | 518.5 | 586.5 | 185.2 | 203.8 |
| 22 | 552.7 | 597.8 | 122.8 | 170.3 |
| 25 | 516.3 | 570.0 | 146.2 | 154.5 |
| 27 | 513.8 | 604.2 | 246.1 | 204.5 |

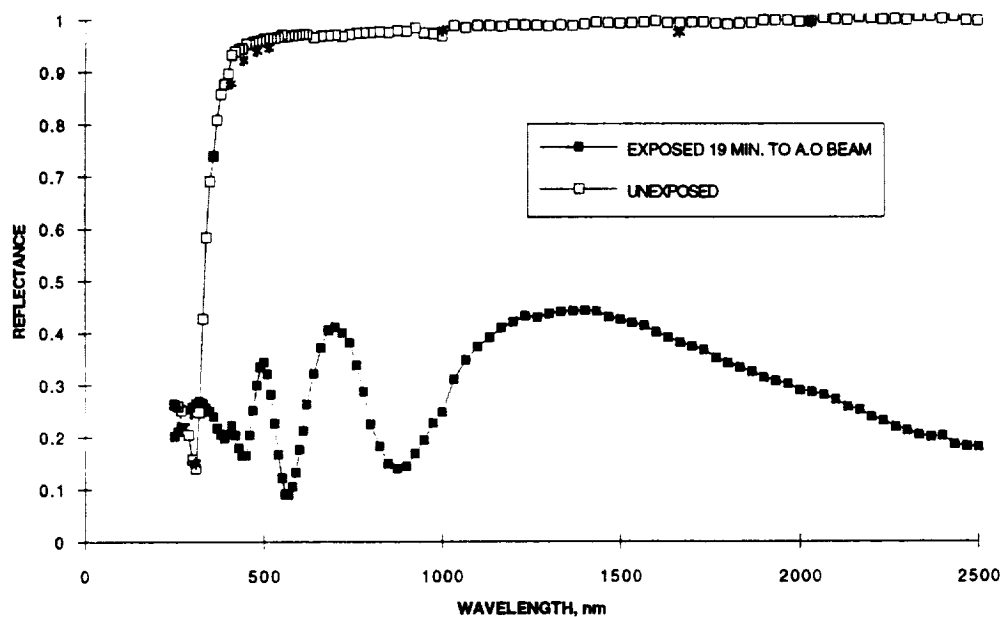


Fig. 1. Measured reflectance of a typical pure silver film compared to calculated values from literature optical constants (*), and the measured reflectance of the same film after conversion to a more transparent oxide exhibiting interference effects.

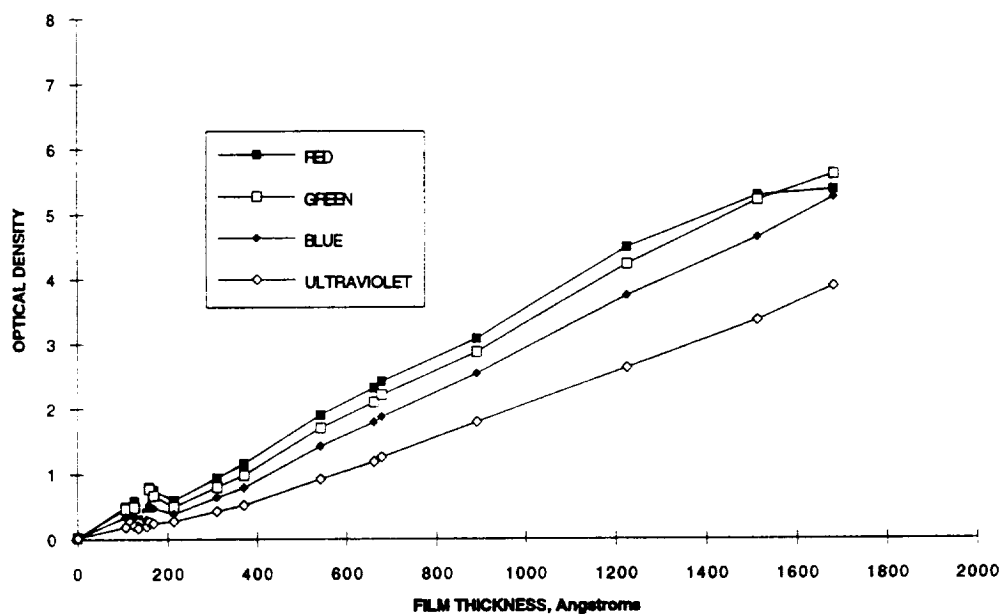


Fig. 2. Measured optical density of pure silver films vs. thickness, showing approximation to Beer's Law for films with strong absorption (interference effects negligible).

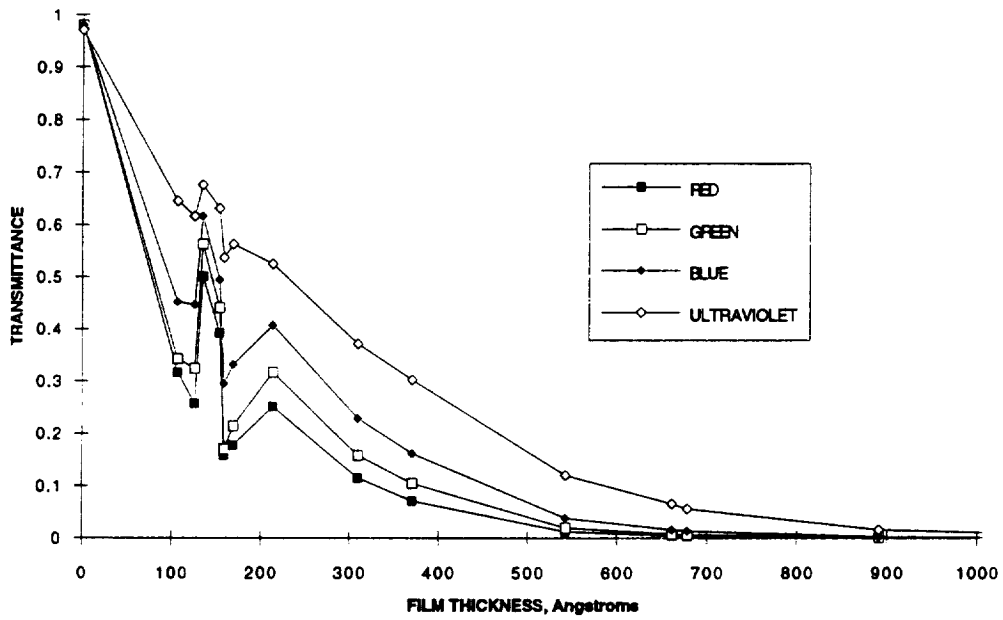


Fig. 3. Measured transmittance vs. film thickness of pure silver on glass. See text for explanation of anomaly near 150 angstroms thickness.

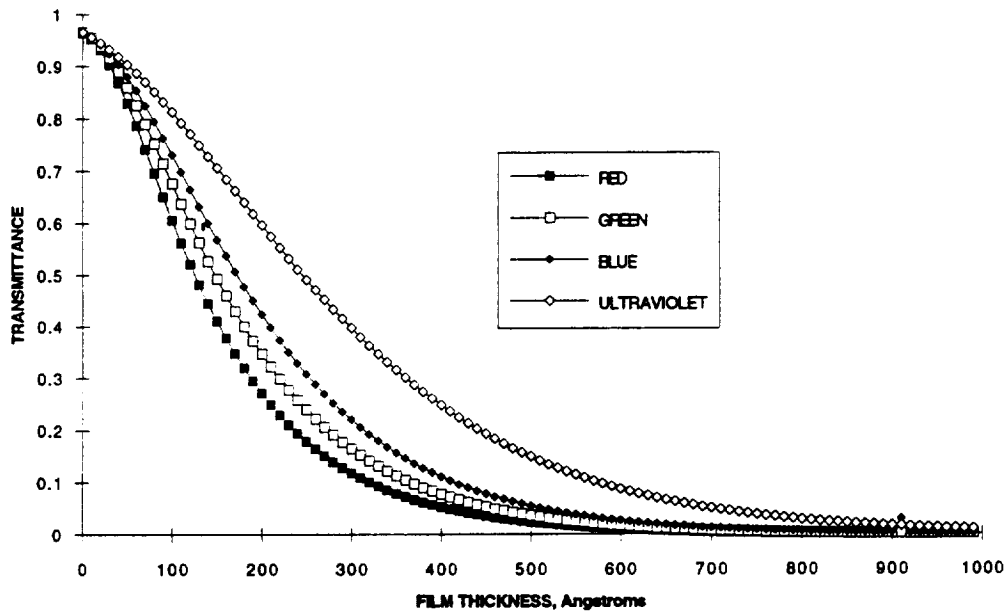


Fig. 4. Calculated transmittance vs. film thickness of pure silver on glass; each curve calculated for a wavelength representative of the middle of the color shown.

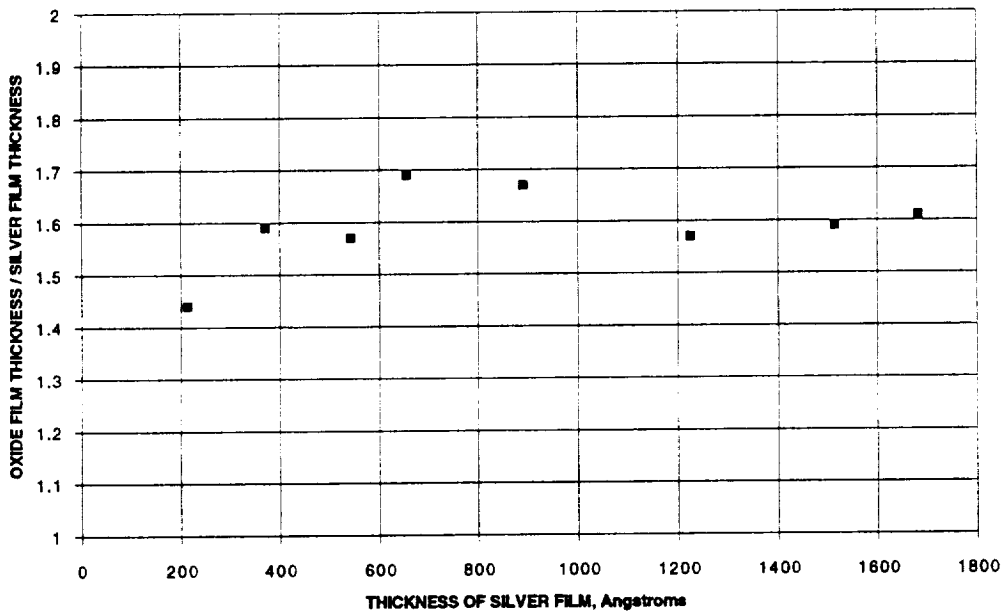


Fig. 5. Expansion in thickness of a number of silver films due to oxidation of sufficient time to convert the whole film to an oxide.

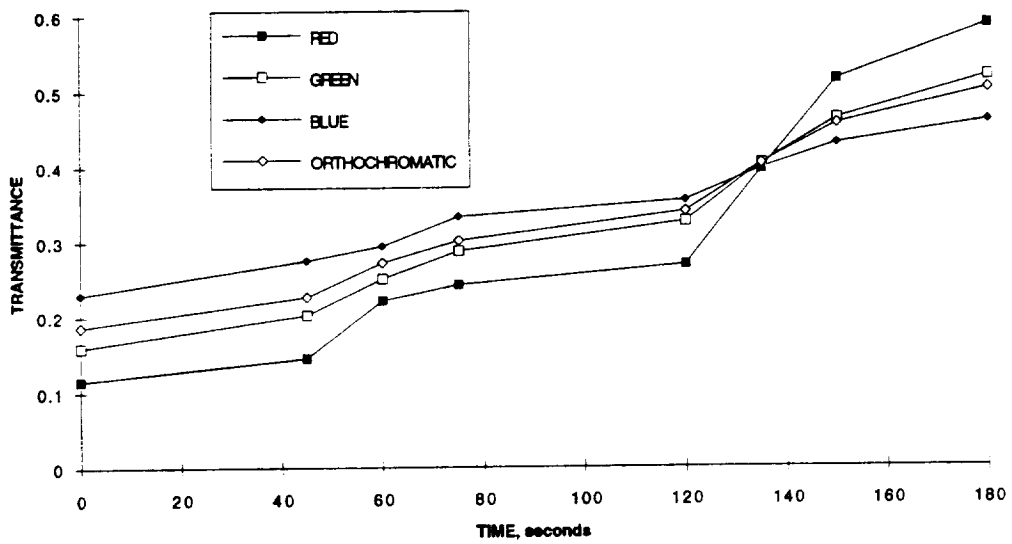


Fig. 6. Measured transmittance vs. exposure time of silver films to oxidation source.

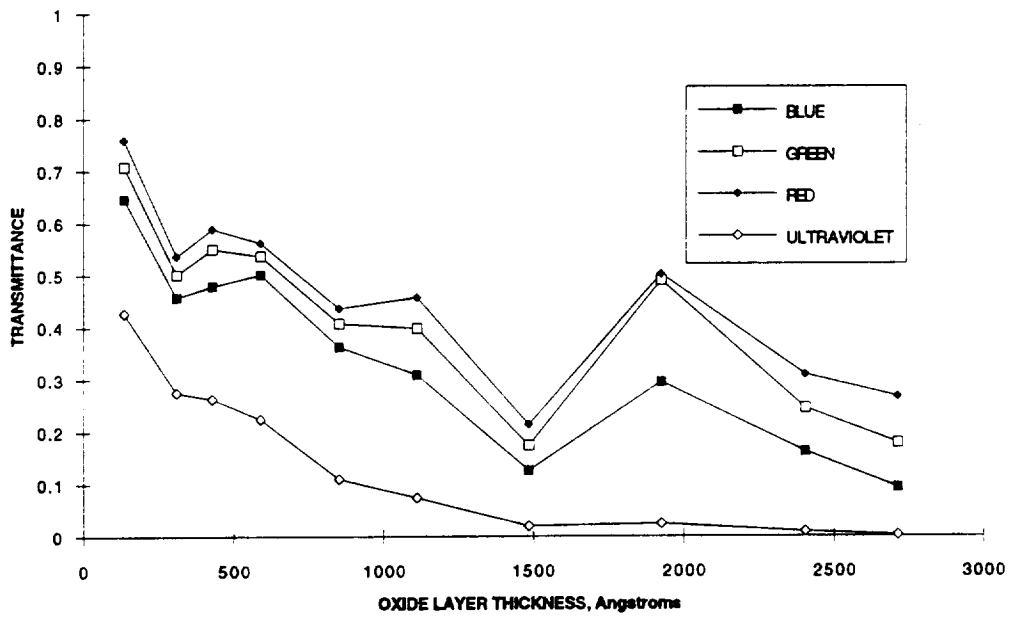


Fig. 7. Measured transmittance vs. silver oxide thickness on glass.

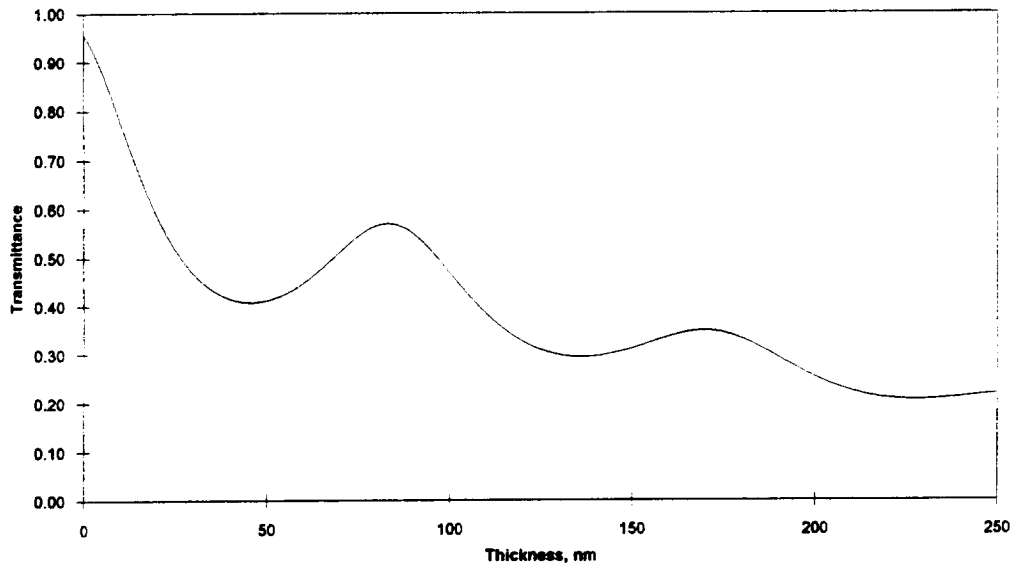


Fig. 8. Calculated transmittance vs. thickness of films for a wavelength of 550 nm, assuming pure silver oxide having $n=3.1$ and $k=0.2$ on glass whose $n=1.53$.

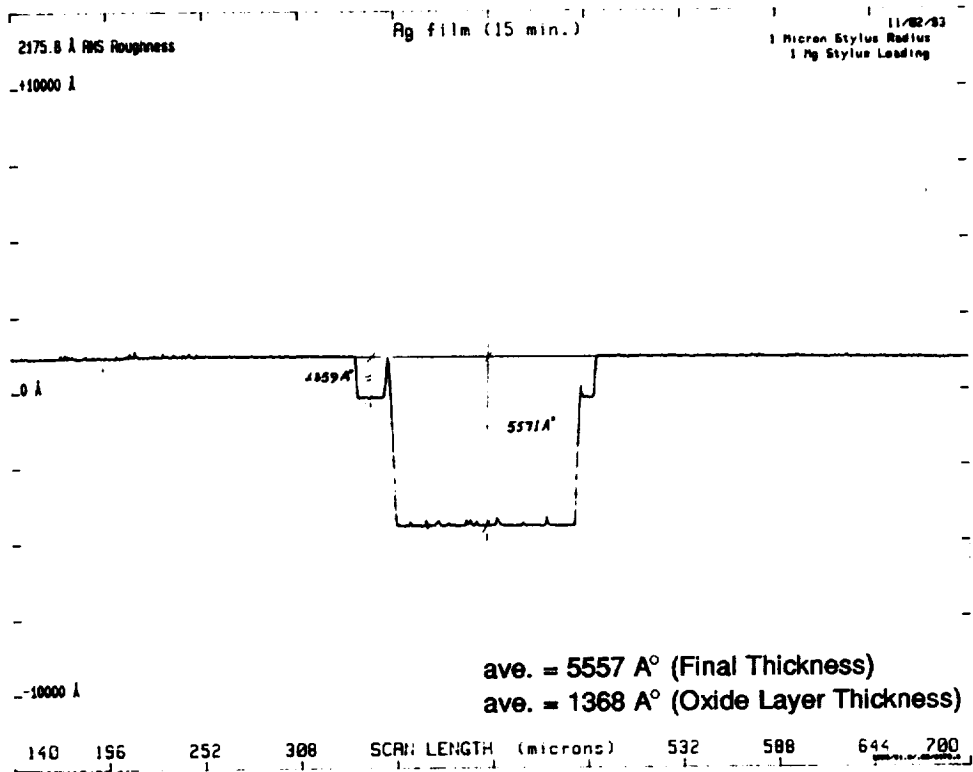


Fig. 9. Stylus profilometry measurement showing typical thickness of one of the thicker films used to measure reflectance of oxide on silver; half of such films exhibited the secondary step interpreted as silver oxide thickness on top of silver.

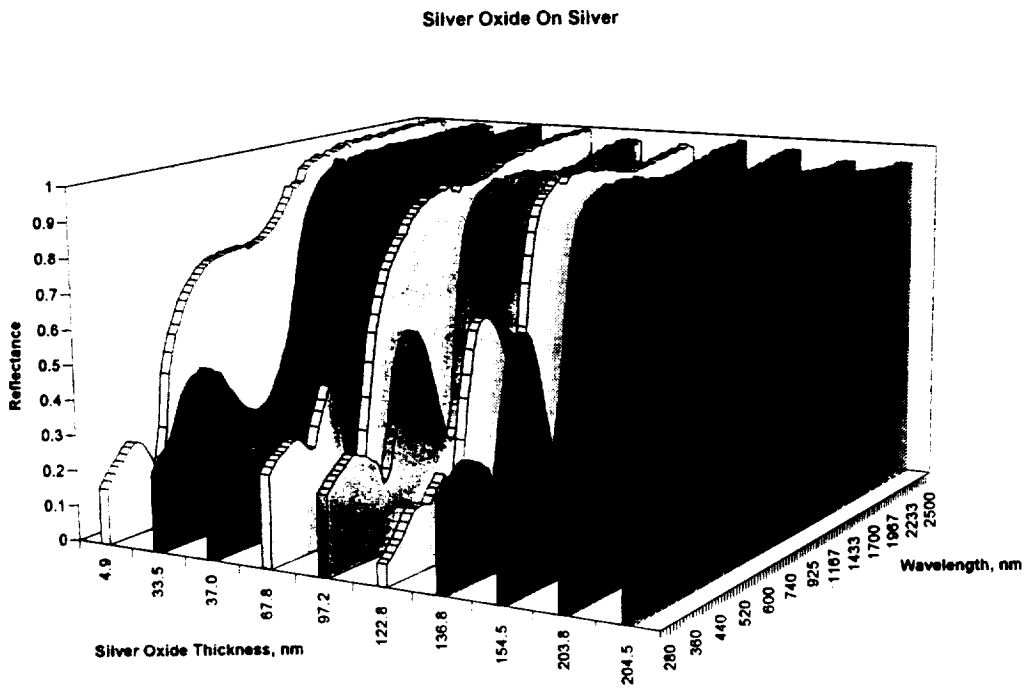


Fig. 10. Reflectance vs. wavelength for ten silver films, all initially thicker than 500 nm, each exposed once for a period ranging from 5 minutes to 27 minutes. See Table and the text for details of estimating silver oxide thickness.

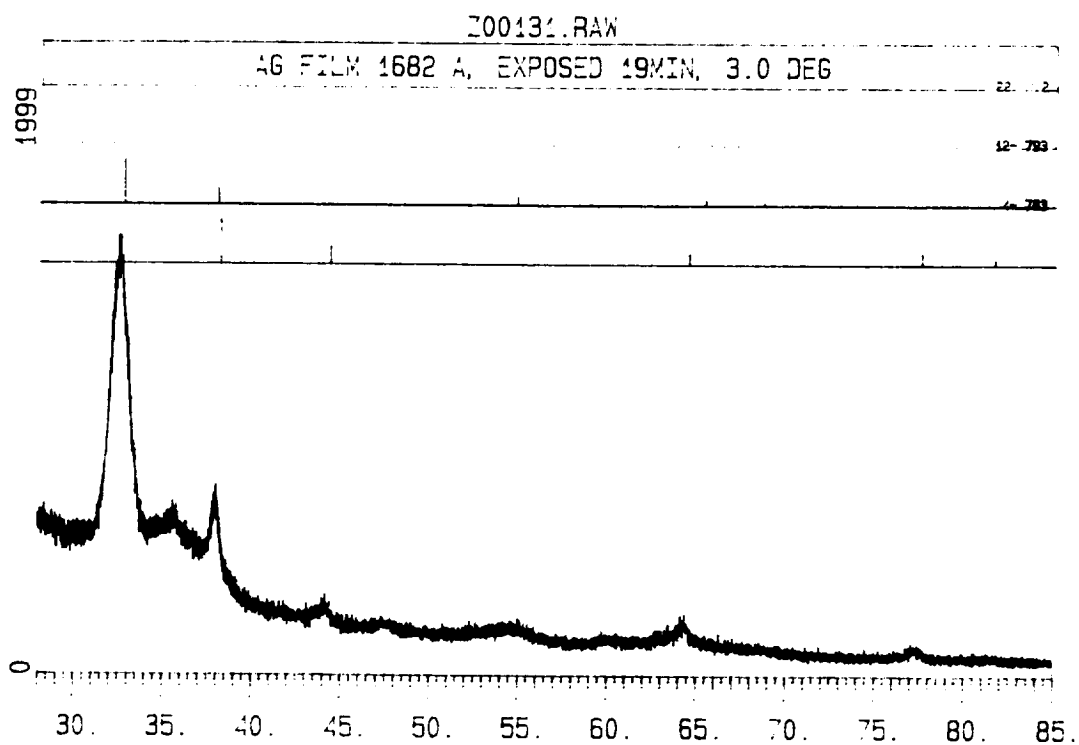


Fig. 11. X-ray diffraction of a silver film, initially 168 nm thick, exposed sufficiently that conversion to silver oxide was assumed. Pattern is most closely represented by Ag_2O .

