CHANGES OF SOME OPTICAL CONSTANTS OF THIN METALLIC FILMS
DUE TO EXPOSURE TO GASES

by

John Wise Sherman, III

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Director of Graduate Studies Head of Department

Dean of Applied Science and Supervisor or Major Professor
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Introduction

When a beam of light is incident on a metallic film, the intensity of the light transmitted in the new medium, or the intensity of the light reflected, is proportional to the intensity of the incident beam. But this proportionality factor is not an absolute constant. This is indicated by the fact that it is different for each type of metal, and depends on the medium through which the light reaches it. It is not even an intrinsic constant for a particular metal, for if the intensity of the incident beam is kept constant, the magnitude of the electric intensity inside the metal, and the magnitude of the electric intensity reflected will be different for different planes of polarization, or for different wavelengths of light, or for different angles of incidence. As it has been pointed out by Fry (16),

"Even if the intensity, color and plane of polarization of the incident light are kept fixed, and only the angle of incident is allowed to change, the curves which relate the intensity inside the metal of the angle of incidence will be of different shapes at different depths below the surface, due to the fact that light is extinguished more rapidly the more oblique its angle of incidence."
Because of the extreme sensitivity of the constants of transmission and reflection (along with the other three optical constants of absorption, index of refraction and the extinction coefficient) to many variables, it is understandable how various independent investigators arrived at values for these optical constants which differ widely from each other.

In the investigation of the optical properties of metal, it must be recalled that the properties of the metal itself differ according to whether the material is in bulk form or a thin film deposited on glass or some other dielectric material.

The study of thin films, rather than the bulk material, is recommendable because the rapid and consistent preparation of thin films is easier than that of the bulk material.

Other variations have been noted (17, 4) by investigators and of these are the changes in optical properties of films in vacuo and air. The purpose of the present work is to try to determine the cause of these changes.
Review of Literature

(1) Historical Sketch. The evaporation technique of preparing thin films was discovered by Phol and Pringsheim in 1912 (20), but not until the early 1930's was the process used in the making of mirrors (3).

Measurements of the optical constants using thin evaporated films were first carried out by O'Bryan in 1935 (25) and by Edward and Petersen in 1936 (17). They revealed quite different constants than previous methods where bulk materials had been polished and measured.

Edward and Petersen performed a similar experiment as was performed in this laboratory, but met difficulty. This occurred when an attempt was made to measure the properties of a magnesium-aluminum film in the presence of pure oxygen. In the words of the authors,

"...the experiment proved to be too dangerous for in one trial an explosion occurred from a rapid oxidation of the oil in the diffusion pumps." (17)

Theoretically, Drude applied the electromagnetic theory to film and crystal optics in the latter part of the 19th century. This theory gave good agreement with experimental work for films thicker than about 200 Å. In 1904 Garnett (28, 13) showed that failure of this theory arose from the
aggregated structure of the thin film.

Fry (14, 15, 16) applied the electromagnetic theory to thin films and in particular, thin metallic films. The theory has been related to the electrical constants and advanced to cover many particular situations.

(2) General Structure of Thin Metallic Films. Evaporated metallic films when sufficiently thin are in general aggregated in structure. The aggregation, as revealed by Sennett and Scott using the electron microscope (23) depends not only on the type of metallic film, the substrate, and the temperature, but also on the rate of depositing the film. The more slowly a film is formed, the more aggregated its structure for thicknesses over 100 A. They showed that the aggregates of slowly formed silver films tend to grow more in height and become thicker before joining together, whereas the rapidly formed silver films tend to flow out over the surface more uniformly. They concluded that films used for optical work should be rapidly formed.

(3) Techniques of Forming Thin Metallic Films. Thin metallic films can be produced chemically or physically. Chemical methods include electron-deposition, reduction, and thermal decomposition. Physical techniques are sputtering, explosion of metal wires in an inert gas, and thermal evaporation. Of all methods thermal evaporation is the best because it
requires less time and is easier to control. Essentially, the metal to form the thin film is evaporated just as water might be. However, the process is carried out in vacuo for two reasons: first, to prevent the metal from oxidizing; and second, to increase the mean free path of a molecule so that it may travel through a great distance before colliding with another molecule or obstruction.

In order to obtain a more continuous film rather than one of aggregated structure, the evaporation was to be carried out as rapidly as possible.

(4) Determination of the Optical Constants. Many investigators have measured the five optical constants, but their techniques fall into three categories: first, the polarization method used by Drude and Fry (14, 15, 16) which is rather bulky to be included in a vacuum chamber (23); second, interferometric method developed primarily by Hadley and Dennison (18), involving graphic or tediously calculated solutions; and third, photoelectric method, which directly measures the intensity of reflected and transmitted light, and is used by a large number of investigators.

(5) Affect of Air on Thin Metallic Films. As previously stated in the historical sketch, Edwards and Petersen (17) noted differences in the reflectivity and transmissivity of metallic films when in vacuo and when in air. This was
verified by P. E. Cheo working in this laboratory in 1951-52 (5). This change has been attributed by some workers as being a process of oxidation (26), but no experiments as revealed in the available literature indicate conclusively that oxidation caused these changes.
Plan of the Project

The object of this experiment was to determine the three optical constants of thin films of silver and copper in vacuo and in several gases, and to try to determine why these properties change in changing from a vacuum to a surrounding medium of one of these several gases. As definite changes had already been noted for metallic films when in air and when in vacuo (17, 6) the main constituents of air were used separately to determine the true cause of these changes. Air is a mixture of nitrogen, oxygen, and small amounts of other gases. Hence, it was logical to use nitrogen, oxygen and an inert gas, argon, for these studies. Possible reasons for the change are oxidation of the metal, adsorption of the gas by the metal, or a combination of the two. Oxidation would occur only with oxygen while adsorption would occur to some extent for all gases.

Difficulty immediately arises when oxygen is chosen. The danger lies in the mixing of hot vapors from the diffusion pump contained in the pumping system, or from any sealing grease which might have been put into the system. The latter is easily remedied, but the former required careful consideration.

To eliminate the hazard two techniques were considered.
First, the diffusion pump could be turned off and allowed to cool before any oxygen was admitted. Second, a valve could be put between the evaporating chamber and the diffusion pump.

The first method has two primary draw-backs. A considerable amount of time would be lost in cooling and heating the diffusion pump. Also, because of small leaks in the system, the residual gas of the evaporating chamber would become contaminated with air, and no conclusion could be made as to which gases brought about the changes. The second technique had no disadvantages other than the actual construction of such a valve.

It was necessary to have a chamber capable of withstanding a good vacuum and one to which the several gases could be readily admitted. At the same time the chamber must contain the evaporation unit and allow the measurement of the three optical constants. Such a chamber had been previously used (7) and was in satisfactory condition except for the flanges which were severely scarred. The substrate holder was permanently mounted in the previous experiment and it was necessary in this experiment to allow the substrate to rotate from a position of normal incidence to the molecular beam to one of normal incidence to the beam of light.

The three means of measurement discussed previously indicated that direct measurement by a photomultiplier tube was the simplest
and easiest method of the measurement of the constants. Essentially, this method involves a beam of light incident on the surface of the material being studied and the photomultiplier tube being placed in such a position as to measure the light reflected and transmitted from the metallic film.

The photo-current produced by light incident on the photosensitive surface of a photomultiplier tube is proportional to the intensity of the light. Measurement of the optical constants then may be considered that of measuring the photo-current since transmission or reflection by the metallic film alters the intensity of the incident light.

A means of accurately measuring this current became necessary in order that the optical constants could be determined. The instrument used to measure this current had to be capable of measuring at least to three significant figures, to measure currents up to 100 microamperes, and to maintain its calibration.

Combinations of micro-ammeters and wall galvanometers gave the desired range and sensitivity, but as a recording potentiometer became available in the department, it was decided to use this instrument to measure the current by detecting the potential drop across a known resistance. This unit met all the requirements for the photo-current measurement.
Because light is partially polarized when reflected from a surface at any angle, except for an angle of incidence of zero degrees, it was decided that measurements of the transmissivity and reflectivity would be made at as near normal incidence to the thin metallic film as possible, thus eliminating any effects due to polarization.

Measurement of the optical constants required a monochromatic light source of high, steady intensity. A commercial medium-pressure mercury-arc used with a constant voltage transformer and two interference filters of wavelengths of 4047 Å and 4358 Å gave a satisfactory light source.

The gases to be used in the experiment have been noted, and as nitrogen, oxygen, and argon are prepared commercially and stored under high pressure in tanks, a problem was presented in rapidly getting the gas from a pressure of approximately 1800 pounds per square inch into a vacuum of the order of $10^{-4}$ mm of mercury with a resultant pressure near that of the atmosphere. Very pure oxygen could have been admitted to the chamber without the pressure problem by diffusion of oxygen through silver (31), but the problem existed for the other two gases, and hence, it was decided to admit all the gases in the same manner.

Two methods were considered. First, bleeding the gas through a very narrow aperture with a diameter of the order of several gas molecule diameters, and second to reduce the pressure in stages. The second technique was chosen in
preference to the first because it was necessary to admit the
gas quickly in order that a sharp contrast, if such existed,
could be made between the optical constants in vacuo and in a
gas.
Description of Apparatus

The apparatus when completed for this experiment consisted of four major parts: the evaporating system, the optical system, the measuring system, and the gassing unit. Where possible commercial or previously built components were used and will not be discussed in detail. Figures 1 and 2 show two general views of the apparatus.

I. Evaporating System. The evaporating system consisted of a pumping system, vacuum valve, vacuum chamber, and the filament heating circuit. Figure 3 gives a schematic diagram of the evaporating and gassing systems.

A. The Pumping System. The pumping system consisted of a mechanical pump, a three stage diffusion pump, and a cold trap connected in series, and a pressure gauge.

1. The Mechanical Pump. The mechanical pump was a Duo-Seal manufactured by W. M. Welch, Type 1405-B (Serial No. 2932-5). This pump is a two stage type with an ultimate vacuum of $1 \times 10^{-4}$ mm of Hg and was powered by a one-half horsepower General Electric motor.

2. The Diffusion Pump. The diffusion pump was a product of Distillation Products Corporation requiring 200 grams of Octoil S oil and operated at a fore pressure as high as 0.10 mm of Hg, with a power input varying from 90 to 250 watts. It was a water cooled unit and its pumping speed was stated to be 25 liters
FIGURE 1
GENERAL VIEW OF APPARATUS
FIGURE 2
GENERAL VIEW OF APPARATUS
FIGURE 3
EVAPORATING & GASSING SYSTEM
sec $^{-1}$ at $10^{-4}$ mm of Hg. The mechanical and diffusion pumps were run continuously in series for two days and a vacuum with a pressure of $2 \times 10^{-6}$ mm of Hg was produced.

3. The Cold Trap. The cold trap was constructed of Pyrex glass and placed immediately after the diffusion pump. The cold trap was covered with braided copper wire and the entire unit submerged in liquid air whenever the vacuum system was used. The copper wire provided a heat exchange medium between the liquid air and the cold trap when the liquid air had evaporated to a point below the glass trap, thus making a charge of liquid air contained in a 1 liter Dewar flask last 6 to 8 hours. Although the cold trap did not increase the pumping speed, it did lower the ultimate vacuum.

4. Pressure Guage. A Phillips Pressure Guage (type PHG-09) manufactured by Consolidated Vacuum Corporation was connected between the cold trap and the vacuum valve and measured pressures from $5 \times 10^{-1}$ to $1 \times 10^{-7}$ mm of Hg on four scales.

B. The Vacuum Valve. A vacuum valve capable of physically supporting the vacuum chamber and also making a good vacuum seal between the vacuum chamber and diffusion pump was required. The technique of inserting "O" rings into a gate valve was employed (24). The valve selected was a 2 inch Crane gate valve, type 440. Figure 4 shows a cross-sectional view of the valve and its adaptor for the vacuum chamber.
FIGURE 4
CROSS-SECTION OF VACUUM VALVE
AND ADAPTOR

SCALE: 1" = 4"
C. The Vacuum Chamber. The vacuum chamber was a previously built unit (8) and only the modifications will be described. As previously stated the flanges were severely scarred and had to be polished with successively finer grades of carborundum in order that the flanges would make a good vacuum seal. All three windows shown in Figure 5 were removed, cleaned, and resealed with Apiezon W wax. Window $W_1$ was resealed so that the normal to this window made a five degree angle with the incident beam. The substrate holder was mounted on a Fafnir bearing, which had been thoroughly cleaned of all oil and grease by soaking in acetone, and a new adaptor made for the substrate holder so that 32 mm diameter glass substrates could be used instead of the previous 44.5 mm substrates. Four small Alnico cylindrical bar magnets were fastened on an aluminum arm and attached to the substrate holder in such a manner that the holder could be rotated externally with another magnet. The two positions of the substrate holder used in the experiment are shown in Figures 6 and 7. Originally, two electrodes were permanently mounted on the chamber itself. One electrode was continuous with the chamber and the other insulated and water-cooled. This latter electrode gave trouble for it was sealed with Apiezon W wax and this leaked when the high current required for the filament heated the electrodes. As shown in Figure 5, the electrode was permanently mounted in the filament cover plate and was constructed of a three-eights inch brass bolt.
FIGURE 5
VACUUM CHAMBER

WINDOW W-1

WINDOW W-2

WINDOW W-3

ELECTRODE

COVER PLATE GASKET

ELECTRODE FILAMENT

MAGNETS

SUBSTRATE HOLDER

SCALE: 1" = 2"
FIGURE 6. SUBSTRATE NORMAL TO MOLECULAR BEAM

FIGURE 7. SUBSTRATE NORMAL TO INCIDENT LIGHT
that would carry high current without heating. Window \( W_3 \) was not used in this experiment.

D. The Filament Heating Circuit. The filament used for evaporation was heated by sixty cycle current at approximately 10 volts. The current was supplied by a step-down transformer which had a variable resistor connected in the primary circuit so that the output current could be varied. Currents used for evaporation were around fifty amperes. Figure 8 shows this circuit, and Figures 6 and 7 show the location of the filament in the evaporating chamber.

II. The Optical System. The optical system consisted of a light source, intensity controlling and collimating unit, filters, and a beam splitting device. Figure 9 give a ray trace through the optical system, and Figure 10 shows a photograph of the optical system.

A. The Light Source. A Hanovia mercury arc (Cat. No. 5043) was used as the light source. This is an alternating current arc with the pressure sufficiently low so that the spectrum is still predominantly a line spectrum with a slight amount of continuous background. To avoid variations of the line voltage a General Electric constant voltage transformer was used to supply the arc voltage.

B. Intensity Controlling and Collimating Unit. This unit's purpose was to vary the intensity of the incident beam on the
FIGURE 8
FILAMENT HEATING CIRCUIT
FIGURE 9

RAY TRACE THROUGH OPTICAL SYSTEM
FIGURE 10. VIEW OF OPTICAL SYSTEM

FIGURE 11. VIEW OF BEAM SPLITTING PRISM
film in question and to render the light beam parallel. This was carried out by focusing light emerging from the source on to an adjustable diaphragm by means of condensing lens. With the diaphragm at the focal point of this condensing lens, the intensity of the light could be varied by varying the diaphragm aperture without affecting the purpose of the collimating lens. The collimating lens was placed so that the diaphragm was at its principal focus. This rendered the emerging light parallel.

C. The Filters. Two Bausch and Lomb interference filters, which transmitted the spectrum lines of 4358 Å and 4047 Å of the Mercury arc, gave an intense monochromatic light source. These filters measured two inches square and for protection from being scarred or scratched were covered with thin plexiglass. In order that these filters transmit the given wavelengths it is necessary for them to be normal to the incident beam. For this reason the two filters were rigidly mounted on a circular disk which was placed in such a manner that the filters could be rapidly rotated into or out of the incident beam and remain at all times normal to the beam.

D. The Beam Splitting Device. A double prism forming a one inch cube was used to split the incident beam in the manner shown in Figure 9 so that the incident beam could be measured as well as the light transmitted and reflected. Figure 11 shows the beam splitting prism. This particular arrangement was made so that the reflectivity could be measured as near zero incidence
as possible. A mechanical advantage existed by using this technique since all apparatus involved in the optical or measuring system were fixed and did not require movement in order that any particular measurement might be made. Because the systems were not disturbed the measurements proceeded rapidly.

III. The Measuring System. The measuring system consisted of two photomultiplier tubes, a D. C. power supply, a standard resistance, and a recording potentiometer.

A. The Photomultiplier Tubes. Two photomultiplier tubes, one 931-A and the other a 1P21, were used. The position of the tubes is shown in Figure 9. A 1P22 was also considered, but sensitivity, rather than heavy current loads, was most important so this tube was not used. The 931-A photomultiplier and 1P21 photomultiplier both have the same spectral response and physical design. They both are sensitive to light in the region from 3000 A to 6000 A with a peak at 4000 ± 500 A, and consist of eleven electrodes. Maximum voltage which could be applied to these tubes was 1250 volts.

B. The D. C. Power Supply. The power supply was a 1000 volt output, direct current supply. It was a previously built unit (9) employing a voltage doubling circuit using two 2 x 2/879 half-wave rectifier tubes and at the output a voltage regulating circuit consisting of eight gas-filled V—R tubes connected in
series. This power pack supplied a steady voltage of 1000 volts to the voltage dividing resistors for the photomultiplier tube dynodes. These dividing resistors and the circuit diagram are given in Figure 12 for the power supply.

C. The Standard Resistance. This resistor was a 100 ohm resistor in series with the photo-current circuit. The resistor was measured on a Leeds and Northrup Wheatstone bridge and found correct to a hundredth of an ohm. The potential drop produced across this resistor due to the photo-current was measured on a recording potentiometer.

D. The Recording Potentiometer. The recording potentiometer was a Weston Model 67001 Recorder, which is of the null-balancing (potentiometer) type, employing a line driven synchronous converted and amplifier to control a two phase motor and re-balance measuring circuit. The time to cross the chart was 1-1/2 seconds and the recorder had automatic or semi-automatic standardization. Accuracy was given as ± 1/4 per cent on ranges above 10 millivolts.

IV. The Gassing Unit. The gassing unit consisted of a mechanical pump, a gas storage tank, pressure guages, a small compressor, a jet valve, and appropriate gases. Figure 3 gives a schematic diagram of the arrangement of this apparatus.

A. The Mechanical Pump. The mechanical oil pump was a Cenco-Megavac, a product of Central Scientific Company with a stated ultimate vacuum of $10^{-4}$ mm of Hg. The purpose of this pump was
FIGURE 12. POWER SUPPLY AND PHOTOMULTIPLIER CIRCUITS
KEY TO FIGURE 12

R₁ - R₁₀ = 58,000 OHMS
R₁₁ - R₁₉ = 39,000 OHMS
R₂₀ = 58,000 OHMS
R₂₁ = 10,000 OHMS
Rₛ = 100.0 OHMS
L₁ = 15 HENRIES
L₂ = 15 HENRIES
C₁ = 1 MICROFARAD, 2000 V.
C₂ = 2 " , 1750 V.
C₃ = 10 " , 3000 V.
VR - 3 - 150 V, 4 - 105 V, 1 - 90 V.
two-fold. First, it served to pump the storage tank to a mo-
derate vacuum before any of the gases (except air) were admitt-
ed to the tank, thus allowing the tank to be flushed and the
original purity of the gases maintained; second, with the
storage tank sealed-off, the vacuum chamber (see Figure 3)
could be pumped through the jet valve to a pressure of $4 \times 10^{-2}$
mm of Hg, sufficient to allow the vacuum valve to be opened
and the pumping system to take-over without the diffusion pump
operating at too high a pressure.

B. The Gas Storage Tank. This tank was a ten inch diameter
iron pipe with a one inch steel plate welded to the bottom,
flanged at the top, and fitted with a rubber gasket and an-
other one inch steel cover plate. The volume of the tank was
around 5 cubic feet. The purpose of the tank was to allow
gas to be bled at high pressure to atmospheric pressure pre-
paratory to entering the vacuum chamber.

C. The Pressure Guages. Two pressure guages were employed.
The first was a McCleod guage covering the interval from 1 to
5000 microns of Hg. The second was a pressure guage calibrated
to read the interval from 0 to 60 pounds per square inch
(absolute). The arrangement of these guages are shown in Figure 3.

D. The Compressor. The compressor was a small unit used only
with oxygen to flush the lines and the vacuum chamber after the
completion of measurements on a film. It produced a maximum
pressure of 10 psi over atmospheric pressure. Nevertheless, it served well to flush the line with air.

E. The Jet Valve. This was a one-eighth inch brass valve used to rapidly admit the gases into the chamber. The location of this valve is shown on Figure 4. The time required to bring the vacuum chamber pressure to atmospheric was eight to ten seconds.

F. The Gases. All gases, except air, were commercially prepared. Nitrogen was the oil-pumped grade supplied by the Southern Oxygen Company. The oil-pumped nitrogen contained a negligible amount of water vapor but may have contained oil vapors. Argon with a purity of 99.6 per cent was used and was supplied by the Ohio Chemical and Surgical Equipment Company. The oxygen was prepared by the Southern Oxygen Company and had a minimum purity of 99.5 per cent.
Experimental Procedure

I. Verification of Weston Recorder Calibration. A check was made on the Weston Recorder to test the potentiometer circuit and standardization of the instrument. The test was made with a Leeds and Northrup Type K-2 potentiometer. The data is shown in Table 1. No curves of correction factors were plotted because it was felt that the errors were random and not systematic, since the actual setting of the potentiometer on a predetermined value was quite difficult.

Table 1 - Test of the Weston Recorder Calibration

<table>
<thead>
<tr>
<th>Indicated Current (uamp)</th>
<th>Actual Current (uamp)</th>
<th>Indicated Current (uamp)</th>
<th>Actual Current (uamp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.04</td>
<td>10.00</td>
<td>10.06</td>
</tr>
<tr>
<td>2.00</td>
<td>2.07</td>
<td>12.00</td>
<td>12.04</td>
</tr>
<tr>
<td>3.00</td>
<td>3.01</td>
<td>14.00</td>
<td>14.09</td>
</tr>
<tr>
<td>4.00</td>
<td>4.02</td>
<td>16.00</td>
<td>16.10</td>
</tr>
<tr>
<td>6.00</td>
<td>6.05</td>
<td>18.00</td>
<td>18.12</td>
</tr>
<tr>
<td>8.00</td>
<td>8.02</td>
<td>19.00</td>
<td>19.36</td>
</tr>
</tbody>
</table>

II. Test of Linearity of the Photomultiplier Tubes and Circuit. The 1P21 and 1P22 displayed high instability when first used in the circuit. As the two tubes were new it was felt that the instability could be corrected by loading the tubes with a high current for an extended period. This was done and the
situation corrected. The linearity of these two tubes and the 1P22 were checked by using the inverse square law. This was performed by using an illuminated ground glass covered pinhole of 0.040 inch diameter as a point source. The photo-current was measured as a function of distance from the source, and this current plotted against the reciprocal of the square of the distance. In order that the current did not exceed that recommended for the tubes, a filter of slightly exposed film was used on the 931-A and 1P21 photomultiplier tubes. Table 2 gives the results of this test, but only the average values of current are given in the table since several runs were made on each tube. A plot of the results are shown on Graph 1.

III. Calibration of 1P21 Filter. Because the 1P21 seemed to be the most sensitive of the three photomultiplier tubes, it was decided to use it in the position covering the most extreme values, this being the photomultiplier tube measuring the incident beam and the reflected beam. Since the incident beam would be of high intensity, a filter was used. Measurements were made for both wavelengths and the results shown in Table 3. The error quoted here is the probable error, and for the definition of this error see the discussion of error in measurements in the following section.
LINEARITY OF PHOTOMULTIPLIER TUBES

CURRENT IN UAMPS

D^{-2} \times 10^{-3} \text{ IN CM}^{-2} (D = \text{DISTANCE})
Table 2 - Linearity of Photomultiplier Tubes

<table>
<thead>
<tr>
<th>Distance (cm)</th>
<th>(D^{-2} \times 10^{-3}) (cm(^{-2}))</th>
<th>931-A (uamp)</th>
<th>1P22 (uamp)</th>
<th>1P21 (uamp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0.494</td>
<td>13.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.400</td>
<td>11.09</td>
<td>16.98</td>
<td>15.50</td>
</tr>
<tr>
<td>55</td>
<td>0.331</td>
<td>9.33</td>
<td>13.78</td>
<td>12.67</td>
</tr>
<tr>
<td>60</td>
<td>0.278</td>
<td>7.95</td>
<td>11.45</td>
<td>10.47</td>
</tr>
<tr>
<td>65</td>
<td>0.237</td>
<td>6.78</td>
<td>9.73</td>
<td>8.95</td>
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<tr>
<td>70</td>
<td>0.204</td>
<td>5.93</td>
<td>8.43</td>
<td>7.61</td>
</tr>
<tr>
<td>80</td>
<td>0.156</td>
<td>4.40</td>
<td>6.38</td>
<td>5.74</td>
</tr>
<tr>
<td>90</td>
<td>0.123</td>
<td>3.72</td>
<td>4.97</td>
<td>4.50</td>
</tr>
<tr>
<td>100</td>
<td>0.100</td>
<td>3.02</td>
<td>4.00</td>
<td>3.53</td>
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<tr>
<td>110</td>
<td>0.083</td>
<td>2.50</td>
<td>3.29</td>
<td>2.93</td>
</tr>
<tr>
<td>120</td>
<td>0.069</td>
<td>2.14</td>
<td>2.76</td>
<td>2.46</td>
</tr>
<tr>
<td>130</td>
<td>0.059</td>
<td>1.85</td>
<td>2.33</td>
<td>2.13</td>
</tr>
<tr>
<td>140</td>
<td>0.051</td>
<td>1.60</td>
<td>1.96</td>
<td>1.81</td>
</tr>
<tr>
<td>150</td>
<td>0.044</td>
<td>1.40</td>
<td>1.68</td>
<td>1.62</td>
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<tr>
<td>160</td>
<td>0.039</td>
<td>1.24</td>
<td>1.49</td>
<td>1.46</td>
</tr>
<tr>
<td>170</td>
<td>0.035</td>
<td></td>
<td>1.32</td>
<td>1.30</td>
</tr>
</tbody>
</table>

IV. Error in Measurements. Errors in the study of the changes of optical properties of metallic thin films were considered as being random rather than systematic. For this reason they lent themselves to statistical treatment. The error assigned to the various values in this work is the probable error
### Table 3 - Calibration of LP21 Filter

<table>
<thead>
<tr>
<th>Wavelength 4358 Å</th>
<th>Without Filter</th>
<th>With Filter</th>
<th>Ratio</th>
<th>Wavelength 4047 Å</th>
<th>Without Filter</th>
<th>With Filter</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µm</td>
<td>µm</td>
<td></td>
<td></td>
<td>µm</td>
<td>µm</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>0.62</td>
<td>6.45</td>
<td></td>
<td>4.42</td>
<td>0.65</td>
<td>6.80</td>
<td></td>
</tr>
<tr>
<td>6.13</td>
<td>0.95</td>
<td>6.45</td>
<td></td>
<td>5.20</td>
<td>0.78</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>7.97</td>
<td>1.23</td>
<td>6.48</td>
<td></td>
<td>5.30</td>
<td>0.90</td>
<td>6.78</td>
<td></td>
</tr>
<tr>
<td>8.25</td>
<td>1.30</td>
<td>6.35</td>
<td></td>
<td>6.90</td>
<td>1.00</td>
<td>6.90</td>
<td></td>
</tr>
<tr>
<td>9.10</td>
<td>1.45</td>
<td>6.28</td>
<td></td>
<td>8.00</td>
<td>1.15</td>
<td>6.95</td>
<td></td>
</tr>
<tr>
<td>9.90</td>
<td>1.62</td>
<td>6.11</td>
<td></td>
<td>9.20</td>
<td>1.38</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>10.25</td>
<td>1.67</td>
<td>6.14</td>
<td></td>
<td>10.12</td>
<td>1.50</td>
<td>6.74</td>
<td></td>
</tr>
<tr>
<td>11.15</td>
<td>1.79</td>
<td>6.23</td>
<td></td>
<td>11.15</td>
<td>1.70</td>
<td>6.56</td>
<td></td>
</tr>
<tr>
<td>12.25</td>
<td>2.03</td>
<td>6.03</td>
<td></td>
<td>12.30</td>
<td>1.82</td>
<td>6.76</td>
<td></td>
</tr>
<tr>
<td>14.25</td>
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<td>6.33</td>
<td></td>
<td>13.22</td>
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<td>6.68</td>
<td></td>
</tr>
<tr>
<td>15.95</td>
<td>2.40</td>
<td>6.65</td>
<td></td>
<td>14.10</td>
<td>2.12</td>
<td>6.65</td>
<td></td>
</tr>
<tr>
<td>16.92</td>
<td>2.50</td>
<td>6.77</td>
<td></td>
<td>15.15</td>
<td>2.30</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td>17.05</td>
<td>2.51</td>
<td>6.79</td>
<td></td>
<td>16.05</td>
<td>2.40</td>
<td>6.69</td>
<td></td>
</tr>
<tr>
<td>17.50</td>
<td>2.58</td>
<td>6.78</td>
<td></td>
<td>17.10</td>
<td>2.60</td>
<td>6.58</td>
<td></td>
</tr>
<tr>
<td>17.95</td>
<td>2.70</td>
<td>6.57</td>
<td></td>
<td>18.15</td>
<td>2.85</td>
<td>6.37</td>
<td></td>
</tr>
<tr>
<td>18.90</td>
<td>2.80</td>
<td>6.75</td>
<td></td>
<td>19.29</td>
<td>2.94</td>
<td>6.56</td>
<td></td>
</tr>
</tbody>
</table>

**Average:** 6.45 ± .25  
**Average:** 6.68 ± .10
defined as (29)

\[ \text{Probable error} = 0.6745 \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots + d_k^2}{k - 1}} \]

where \( d \) is the deviation from the average value of each individual value and \( k \) is the number of observations made in determining the average value. The probable error was the most conservative of the several types of error which could have been used. Although it was not possible to assign errors to the actual measured values of transmissivity, reflectivity, etc., because they were functions of time and could not be repeated for any one film of a given thickness, errors could be assigned to the calibration of the system and thus give an idea of the accuracy of the apparatus. The complete process of determining the probable error has been carried out in Table 7 in order to show the procedure followed.

V. Relation Between Photomultiplier Tubes. Since two photomultipliers were used it was necessary to know the current relationship between them. As photo-current may vary for the same intensity, equal area of exposure, but different positions of exposure of the sensitive element of these photomultiplier tubes, it was necessary to determine the relationship with the photomultiplier tubes mounted as they would be used in the experiment. The photomultiplier tubes were housed in light tight cases, one case being a commercial unit and the other
Table 4 - Relation Between 931-A and 1P21 Photomultiplier Tubes

<table>
<thead>
<tr>
<th>Wavelength 4358 A</th>
<th></th>
<th>Wavelength 4047 A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>931-A (uamp)</td>
<td>1P21 (uamp)</td>
<td>Ratio</td>
<td>931-A (uamp)</td>
</tr>
<tr>
<td>3.9</td>
<td>10.2</td>
<td>2.62</td>
<td>2.0</td>
</tr>
<tr>
<td>6.4</td>
<td>15.5</td>
<td>2.42</td>
<td>4.2</td>
</tr>
<tr>
<td>8.2</td>
<td>20.0</td>
<td>2.43</td>
<td>5.0</td>
</tr>
<tr>
<td>10.2</td>
<td>24.5</td>
<td>2.40</td>
<td>6.2</td>
</tr>
<tr>
<td>12.5</td>
<td>30.5</td>
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<td>8.4</td>
</tr>
<tr>
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<td>35.8</td>
<td>2.45</td>
<td>10.3</td>
</tr>
<tr>
<td>16.5</td>
<td>40.5</td>
<td>2.45</td>
<td>10.2</td>
</tr>
<tr>
<td>18.3</td>
<td>44.8</td>
<td>2.45</td>
<td>12.2</td>
</tr>
<tr>
<td>20.2</td>
<td>50.8</td>
<td>2.51</td>
<td>14.5</td>
</tr>
<tr>
<td>25.0</td>
<td>60.6</td>
<td>2.42</td>
<td>15.0</td>
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<tr>
<td>28.0</td>
<td>65.8</td>
<td>2.35</td>
<td>16.4</td>
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<tr>
<td>35.0</td>
<td>85.1</td>
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<td>18.3</td>
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<tr>
<td>40.0</td>
<td>98.7</td>
<td>2.47</td>
<td>20.0</td>
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<tr>
<td>44.9</td>
<td>115.5</td>
<td>2.57</td>
<td>22.1</td>
</tr>
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<td>51.3</td>
<td>130.3</td>
<td>2.54</td>
<td>25.1</td>
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<td>54.8</td>
<td>143.8</td>
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<td>28.0</td>
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<td>30.1</td>
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<td>65.0</td>
<td>174.1</td>
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<td>35.4</td>
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<tr>
<td>70.0</td>
<td>190.3</td>
<td>2.72</td>
<td>40.1</td>
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<td>75.9</td>
<td>207.0</td>
<td>2.73</td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average: 2.52 ± 0.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average: 50.1 ± 131.6</td>
<td></td>
</tr>
</tbody>
</table>
made in this laboratory. Each had an exposure aperture of approximately 1/16 inch, and were permanently mounted in positions. All photo-currents were related to the 1P21 photomultiplier tube. The relationship between the 931-A and 1P21 are shown in Table 4, and the ratio expressed in this table is the ratio of the 1P21 photo-current to the 931-A photo-current.

VI. Measurement of Blank Substrate Optical Constants. With the optical and measuring systems aligned, preliminary measurements were made of the optical constants of the blank glass substrates. Also, it was possible to calibrate the beam splitting prism, by using these constants. Initially, the index of refraction of four arbitrarily selected blank glass substrates was measured, and from this the reflectivity calculated, and then the beam splitting device was calibrated. Also, the transmissivity of the blank glass substrate was measured.

A. Measurement of the Index of Refraction. As it was desired to have data to three significant figures, the technique of focusing a microscope on the surfaces of the medium for which the index of refraction was being determined was sufficient (33). Figure 13 gives the diagram showing the measurements indicated in Table 5. Talcum powder was used on each surface to insure a proper focus. To measure the microscope was focused on a
large glass flat, then b was measured with the glass substrate between the microscope and glass flat (the microscope was again focused on the glass flat). Finally, c was measured by focusing on the talcum powder spread on the top of the glass substrate. It is readily shown that the index of refraction is given by

\[ n = \frac{a - c}{b - c} \]

Table 5 gives the results of the index of refraction. The value of the index of refraction for the wavelength of 4358 Å was measured but not for 4047 Å. This was because of the low intensity of this wavelength, and the lack of sensitivity of the human eye at this wavelength. The error introduced by assuming the index of refraction was the same for both wavelengths was slight, for a check reveals that to three significant figures the index of refraction changes slightly in this region (19).

B. Measurement of the Reflectivity. A result of Maxwell's equations for normal reflection is

\[ R = \frac{(n - n')^2}{(n - n')^2} , \]

where R is the reflection coefficient, n is the index of refraction of the medium reflecting, and \( n' \) is the index of refraction of the surrounding medium. Although it is a theoretical equation, it has been proven accurate and often used to measure reflection where light is incident normally (21).
\[ N = \frac{d_2}{d_1} = \frac{p_2 - c}{p_1 - c} \]

**Figure 13**

MEASUREMENT OF INDEX OF REFRACTION

**Figure 14**

BEAM SPLITTING DEVICE
The result of this equation is shown at the end of Table 5.

Table 5 - Index of Refraction and Reflection Coefficient

<table>
<thead>
<tr>
<th>Substrate Number</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>a - c</th>
<th>b - c</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
<td>mm</td>
</tr>
<tr>
<td>1</td>
<td>2.150</td>
<td>1.997</td>
<td>1.749</td>
<td>0.401</td>
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<tr>
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<td>1.722</td>
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<td>1.710</td>
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<td>2.128</td>
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<td>1.725</td>
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<td>0.379</td>
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<tr>
<td>2</td>
<td>2.129</td>
<td>1.982</td>
<td>1.729</td>
<td>0.400</td>
<td>0.253</td>
<td>1.581</td>
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<td>1.727</td>
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<tr>
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<td>1.986</td>
<td>1.729</td>
<td>0.406</td>
<td>0.257</td>
<td>1.580</td>
</tr>
</tbody>
</table>

Average: n = 1.56 ± 0.04

n' = 1.00

R = 0.0479 ± 0.0050

C. Calibration of the Beam Splitting Device. In Figure 14 is given a ray trace of the Beam Splitting Device. Reflectivity is defined in the Glossary as $I_r / I_o$, where $I_r$ is the intensity of the light reflected, and $I_o$ is the incident intensity. However, in this experiment we had a beam splitting device, which might cause this definition to differ by a constant. Consider Path 2 in Figure 14. Since the transmissivity and absorptivity of the prism and the reflectivity of the mirror are not known, there is no way to measure the true incident

48
intensity. But since transmissivity, absorptivity, and reflectivity are constant for this unit, we do know the true intensity is proportional to the measured intensity. Thus,

\[ I_{o\text{(meas)}} = I_o R_p R_m (1 - R_p)(1 - A_p)^2 \]

\[ R_p = \text{Reflectivity of prism face} \]
\[ R_m = \text{Reflectivity of mirror} \]
\[ A_p = \text{Absorption of prism} \]
\[ I_o = \text{True incident intensity} \]

Using Path 1 it is seen that

\[ I_{r\text{(meas)}} = I_o (1 - R_p)(1 - A_p)^2 R_s R_p \]

Where \[ R_s = \text{Reflectivity of blank substrate} \]

Thus,

\[ R = \frac{I_{r\text{(meas)}}}{I_{o\text{(meas)}}} = \frac{I_o (1 - R_p)(1 - A_p)^2 R_s R_p}{I_o R_p R_m (1 - R_p)(1 - A_p)^2} = \frac{R_s}{R_m} \]

Hence,

\[ R_s = \frac{R_m I_{r\text{(meas)}}}{I_{o\text{(meas)}}} = \frac{I_{r\text{(meas)}}}{C I_{o\text{(meas)}}} \]

If the beam splitting prism in the Figure 14 transmitted 50 per cent of the incident light and reflected 50 per cent from the reflecting surface and if the reflecting mirror (M1) in this figure reflected 100 per cent then the constant C would be identically one. However this is not necessarily the case. Since the photo-current is directly proportional to the intensity, then measurement of the photo-current gives the intensity (except for the difference of a constant). The reflectivity
Table 6 - Evaluation of C.

<table>
<thead>
<tr>
<th>Wavelength 4358 Å</th>
<th>Io (uamp)</th>
<th>Ir (uamp)</th>
<th>Ir / Io</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>106.4</td>
<td>9.8</td>
<td>0.0921</td>
<td>0.961 ± 0.096</td>
</tr>
<tr>
<td></td>
<td>123.8</td>
<td>11.5</td>
<td>0.0930</td>
<td>0.971 ± 0.097</td>
</tr>
<tr>
<td></td>
<td>136.7</td>
<td>13.5</td>
<td>0.0988</td>
<td>1.031 ± 0.103</td>
</tr>
<tr>
<td></td>
<td>158.0</td>
<td>15.2</td>
<td>0.0962</td>
<td>1.004 ± 0.100</td>
</tr>
<tr>
<td></td>
<td>169.6</td>
<td>16.7</td>
<td>0.0985</td>
<td>1.028 ± 0.103</td>
</tr>
<tr>
<td></td>
<td>183.2</td>
<td>17.5</td>
<td>0.0955</td>
<td>0.997 ± 0.099</td>
</tr>
<tr>
<td></td>
<td>199.3</td>
<td>18.8</td>
<td>0.0943</td>
<td>0.984 ± 0.098</td>
</tr>
<tr>
<td></td>
<td>212.9</td>
<td>21.0</td>
<td>0.0986</td>
<td>1.029 ± 0.103</td>
</tr>
</tbody>
</table>

Average: C = 1.001 ± 0.030

<table>
<thead>
<tr>
<th>Wavelength 4047 Å</th>
<th>Io (uamp)</th>
<th>Ir (uamp)</th>
<th>Ir / Io</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>58.1</td>
<td>5.4</td>
<td>0.0929</td>
<td>0.970 ± 0.097</td>
</tr>
<tr>
<td></td>
<td>70.1</td>
<td>7.1</td>
<td>0.1013</td>
<td>1.057 ± 0.106</td>
</tr>
<tr>
<td></td>
<td>84.2</td>
<td>8.8</td>
<td>0.1045</td>
<td>1.090 ± 0.109</td>
</tr>
<tr>
<td></td>
<td>99.5</td>
<td>10.2</td>
<td>0.1025</td>
<td>1.069 ± 0.106</td>
</tr>
<tr>
<td></td>
<td>115.6</td>
<td>11.6</td>
<td>0.1003</td>
<td>1.046 ± 0.105</td>
</tr>
<tr>
<td></td>
<td>131.6</td>
<td>13.6</td>
<td>0.1033</td>
<td>1.078 ± 0.108</td>
</tr>
<tr>
<td></td>
<td>151.0</td>
<td>14.5</td>
<td>0.0960</td>
<td>1.002 ± 0.100</td>
</tr>
</tbody>
</table>

Average: C = 1.045 ± 0.030
of the blank substrate is known, and if Path 1 is used in
Figure 10 the current due to reflection, and thus intensity,
can be measured. Breaking Path 1 and using Path 2 in Figure
10, the incident beam can be measured. Thus, since there are
two reflections

\[ R = \frac{(n - n')^2}{(n + n')^2} = 0.0479 \pm 0.0050 = \frac{I_r}{2I_o}. \]

Hence,

\[ C = \frac{I_r}{I_o \left(2(0.0479 \pm 0.0050)\right)}. \]

Table 6 shows the evaluation of \( C \).

D. Measurement of the Transmissivity. The transmissivity was
measured in a straightforward manner. The transmitted intensity,
\( I_t \), was measured on the 931-A and the incident intensity, \( I_o \),
on the 1P21 as shown in Figure 9. Table 7 and Table 8 shows
the result of these measurements for the two wavelengths.
Transmissivity has been defined in the Glossary.

VII. Preparation for Thermal Evaporation. In order to obtain
an adherent coating of the metallic film on the glass substrate,
the supporting surface must be free from contaminant films such
as grease, adsorbed water, etc.. Holland (22) points out that
a durable film cannot be achieved unless the substrate surface
is void of all types of contaminants and that with the exception
of vapor degreasing, these contaminants cannot be removed by
chemical methods. Only gross surface contaminants may be
removed chemically. However, even if such cleaning techniques
Table 7 - Transmissivity of Blank Substrates at 4358 A

<table>
<thead>
<tr>
<th>Io</th>
<th>It</th>
<th>Transmissivity</th>
<th>d</th>
<th>d^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(uamp)</td>
<td>(uamp)</td>
<td>(in %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62.0</td>
<td>55.7</td>
<td>89.8</td>
<td>1.13</td>
<td>1.28</td>
</tr>
<tr>
<td>77.3</td>
<td>70.3</td>
<td>90.9</td>
<td>2.23</td>
<td>4.97</td>
</tr>
<tr>
<td>94.2</td>
<td>83.9</td>
<td>89.1</td>
<td>0.43</td>
<td>0.18</td>
</tr>
<tr>
<td>102.4</td>
<td>92.2</td>
<td>90.0</td>
<td>1.76</td>
<td>3.10</td>
</tr>
<tr>
<td>116.3</td>
<td>101.9</td>
<td>87.6</td>
<td>1.07</td>
<td>1.14</td>
</tr>
<tr>
<td>125.6</td>
<td>110.3</td>
<td>87.8</td>
<td>0.87</td>
<td>0.76</td>
</tr>
<tr>
<td>130.1</td>
<td>116.7</td>
<td>89.7</td>
<td>1.03</td>
<td>1.06</td>
</tr>
<tr>
<td>141.9</td>
<td>122.6</td>
<td>86.4</td>
<td>2.27</td>
<td>5.15</td>
</tr>
<tr>
<td>148.8</td>
<td>130.3</td>
<td>87.6</td>
<td>1.07</td>
<td>1.14</td>
</tr>
<tr>
<td>156.6</td>
<td>138.7</td>
<td>88.6</td>
<td>0.07</td>
<td>0.00</td>
</tr>
<tr>
<td>164.9</td>
<td>145.1</td>
<td>88.0</td>
<td>0.67</td>
<td>0.45</td>
</tr>
<tr>
<td>170.1</td>
<td>151.6</td>
<td>89.1</td>
<td>0.43</td>
<td>0.18</td>
</tr>
<tr>
<td>177.0</td>
<td>157.4</td>
<td>88.9</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>184.6</td>
<td>162.5</td>
<td>88.0</td>
<td>0.67</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Probable Error of Average = 0.6745 \sqrt{\frac{\sum_{i=1}^{k} d_i^2}{k-1}} = 0.804

Thus the average value of the transmissivity = 88.7 ± 0.8 %
Table 8 - Transmissivity of Blank Substrates at 4047 A

<table>
<thead>
<tr>
<th>$I_0$ (uamp)</th>
<th>$I_t$ (uamp)</th>
<th>Transmissivity (in %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.3</td>
<td>27.7</td>
<td>88.5</td>
</tr>
<tr>
<td>42.4</td>
<td>38.3</td>
<td>90.0</td>
</tr>
<tr>
<td>53.1</td>
<td>47.4</td>
<td>89.3</td>
</tr>
<tr>
<td>63.5</td>
<td>56.1</td>
<td>88.3</td>
</tr>
<tr>
<td>70.2</td>
<td>62.1</td>
<td>88.5</td>
</tr>
<tr>
<td>79.7</td>
<td>70.1</td>
<td>88.0</td>
</tr>
<tr>
<td>88.6</td>
<td>78.2</td>
<td>88.3</td>
</tr>
<tr>
<td>94.7</td>
<td>84.2</td>
<td>88.9</td>
</tr>
<tr>
<td>103.0</td>
<td>91.5</td>
<td>88.8</td>
</tr>
<tr>
<td>109.5</td>
<td>96.2</td>
<td>87.9</td>
</tr>
<tr>
<td>112.6</td>
<td>100.2</td>
<td>89.0</td>
</tr>
<tr>
<td>113.8</td>
<td>103.5</td>
<td>90.9</td>
</tr>
<tr>
<td>120.0</td>
<td>104.9</td>
<td>87.4</td>
</tr>
</tbody>
</table>

as vapor degreasing or ionic bombardment is employed, the problem of keeping the substrates clean in the atmosphere become prominent. For this reason and because durability of the film after evaporation was not too important, it was decided that cleaning the substrates in acetone, washing in a detergent (Tide), rinsing in water, washing the surface with distilled water, and finally force drying with a fan or
drying on a soft clean towel would be sufficient. This seemed to be acceptable because the metallic films adhered uniformly as long as the films were kept. The physical size of the substrates employed in this experiment was approximately 32 mm diameter optical glass blanks of about 4 mm thickness.

VIII. Thermal Evaporation of Metallic Films. The filaments used in this experiment were cylindrical coils of molybdenum wire (supplied by Cenco, Catalog No. 89695) made up of about five turns. With a filament in place and charged with the desired metal, the substrate was placed in the holder and by means of two adjusting screws (10), the substrate was rendered normal to the incident beam (this being indicated when a maximum was reached by the light reflected normally from the substrate). The system was closed at this point. Since during operating periods the pumping system was left in operation by keeping the vacuum valve closed, the jet valve was opened and the vacuum chamber pumped down to a pressure of $4 \times 10^{-2}$ mm of Hg by the mechanical pump in the gassing system. At this point the jet valve was closed and the vacuum valve opened, allowing the pumping system to reduce the pressure in the vacuum chamber still further. When the pressure reached $1 \times 10^{-3}$ mm of Hg, a low filament current was turned on to melt and out-gas the charge of metal on the filament. When the pressure was further reduced to $4 \times 10^{-3}$ mm of Hg, the system was ready for thermal evaporation. With the substrate
normal to the molecular beam path, the current was again turned on with a much higher current of the order of 50 amperes passing through it. At this pressure and filament current the evaporating time varied from 10 to 90 seconds, depending on the thickness of the desired film. Optimum time for reaching the desired vacuum was 20 minutes. The silver used to charge the filament was a No. 18 wire (B & S guage) supplied by Cenco, and the copper wire used was No. 14 guage electrical wire. Both metal wires were cleaned with acetone prior to being placed on the filament.

IX. Preparation of the Optical and Measuring Systems. The mercury arc source was turned on a minimum of 15 minutes (11) before it was desired to make observations on the films, and the measuring system a minimum of 20 minutes for warm-up and stabilization.

X. Preparation of the Gassing System. When necessary to change the gas held in the storage tank it was pumped to a pressure of several hundred microns and flushed with the gas to be used next. Then it was pumped again to the same approximate vacuum and filled with the same gas (except the system was not flushed with oxygen, since it was considered dangerous to pump pure oxygen through the oil in the pump). The pressure inside the gas storage tank was maintained at atmospheric pressure or a little above in order that the gas contained therein would not
become contaminated. At the desired time after evaporation the vacuum valve was closed and the jet valve opened, thus filling the vacuum chamber.

XI. Measurement of the Three Optical Constants. As soon as the evaporation was completed and the filament current turned off, $I_0$ was set at the value of 30 uamps using the filter, which corresponded to a current of 193.5, at the wavelength of 4358 Å. The constants were measured several times in vacuo, the vacuum valve closed, and the jet valve opened and the recorder started simultaneously. The recorder ran continuously during the run, while values of $I_r$ and $I_t$ were measured for both wavelengths. The incident beam, $I_0$, was measured frequently during the process, and if the value of $I_0$ did not remain constant, the values of $I_r$ and $I_t$ were ruled void between the interval of varying $I_0$. The beam breaking necessary to make the several measurements were carried out by using small non-reflecting black cards, which interrupted the necessary light beams quickly and effectively.
Data, Calculations, and Curves

I. Data. Data in this experiment has been omitted from the thesis because of its length. This is obvious when it is considered that there are approximately 6000 points plotted on the following curves. The original recorded charts, along with the calculations of transmissivity and reflectivity, are available in this laboratory.

II. Calculations. The definitions of transmissivity, reflectivity, and absorptivity may be found in the glossary. All of these quantities are ratios and the calculations, once certain corrections were made, were simple since an electric calculating machine was available. The difficult part was the actual reading of the charts since so many points were involved. In order that the calculations might be done in a minimum of time once the charts had been read, a table was prepared of constants for finding the various quantities. Table 9 lists these constants. It must be remembered that the glass substrates also have transmission, reflection, and absorption. Hence a correction was necessary for the glass substrates. The correction for the blank substrates is also included in Table 9. If figure 15 is consulted the corrections may be better understood. In the figure the incident beam had been at some angle of incidence other than normal, but the case applies to normal reflection and transmission. In this
figure let the symbols be defined as follows:

\[
\begin{align*}
I_0 &= \text{intensity of the incident beam} \\
I_t &= \text{intensity of the transmitted beam} \\
I_r &= \text{intensity of the reflected beam} \\
I_{gt} &= \text{intensity of the beam transmitted through the glass substrate only} \\
I_{gr} &= \text{Intensity of the reflected beam from the surface of the glass substrate only} \\
T_g &= \text{transmissivity of the glass substrate} \\
R_g &= \text{reflectivity of the glass substrate} \\
T &= \text{transmissivity of the metallic film} \\
R &= \text{reflectivity of the metallic film}
\end{align*}
\]

From Figure 15 it is obvious that,

\[
I_t = I_0 T_g
\]

Thus,

\[
T = \frac{I_t}{I_0 T_g}
\]

But,

\[
T_g = \frac{I_g}{I_0}
\]

Therefore,

\[
T = \frac{I_t}{I_{gt}}
\]

Since the reflected beam consisted of two parts,

\[
I_r = I_0 R + I_0 T^2 R_g
\]

Thus,

\[
R = \frac{I_r}{I_0} - T^2 R_g
\]

But,

\[
R_g = \frac{I_{gr}}{I_0}
\]

Therefore,

\[
R = \frac{I_r - T^2 I_{gr}}{I_0}
\]

It is to be noted in the derivation of the equation the assumption was made that light was internally reflected only once. This is justified on the basis of the lower reflectivity of glass. The absorptivity, \( A \), was calculated based upon the
**Table 9 - Calculation Constants**

<table>
<thead>
<tr>
<th>Wavelength 4358 A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g = 0.887$</td>
<td></td>
</tr>
<tr>
<td>Filter Ratio = 6.45</td>
<td></td>
</tr>
<tr>
<td>931-A Correction = 2.52</td>
<td></td>
</tr>
<tr>
<td>$C = 1.001$</td>
<td></td>
</tr>
<tr>
<td>$I_o = 193.5$ uamp</td>
<td></td>
</tr>
<tr>
<td>$T^2I_{gr} = 14.6$ uamp</td>
<td></td>
</tr>
<tr>
<td>$I_{gt} = 171.6$ uamp</td>
<td></td>
</tr>
<tr>
<td>$T = (2.52/171.6)I_t$</td>
<td></td>
</tr>
<tr>
<td>$= 0.01469 I_t$</td>
<td></td>
</tr>
<tr>
<td>Without Filter R = (1/(193.5)(1.001) I_r - (14.6/193.5)</td>
<td></td>
</tr>
<tr>
<td>$= 0.005 I_r - 0.075$</td>
<td></td>
</tr>
<tr>
<td>With Filter R = 6.45/(193.5)(1.001) I_r -14.6/193.5</td>
<td></td>
</tr>
<tr>
<td>$=0.0333 I_r - 0.075$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wavelength 4047 A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g = 0.888$</td>
<td></td>
</tr>
<tr>
<td>Filter Ratio = 6.68</td>
<td></td>
</tr>
<tr>
<td>931-A Correction = 2.50</td>
<td></td>
</tr>
<tr>
<td>$C = 1.045$</td>
<td></td>
</tr>
<tr>
<td>$I_o = 89.5$ uamp</td>
<td></td>
</tr>
<tr>
<td>$T^2I_{gr} = 6.77$ uamp</td>
<td></td>
</tr>
<tr>
<td>$I_{gt} = 79.5$ uamp</td>
<td></td>
</tr>
<tr>
<td>$T = (2.50/79.5)I_t = 0.03144 I_t$</td>
<td></td>
</tr>
<tr>
<td>$= 1/(1.045)(89.5) I_r - 6.77/89.5$</td>
<td></td>
</tr>
<tr>
<td>$= 0.01069 I_r - 0.076$</td>
<td></td>
</tr>
</tbody>
</table>
equation,

$$R + T + A = 1.$$  

This relation assumes that there was negligible scattering.

III. Reflectivity, Transmissivity, and Absorptivity of the Films.

By varying the length of time of evaporation of the metal in the filament the thickness of the films deposited on the glass substrate was controlled. A distribution of various thicknesses was made for each of vacuum-to-gas films. Each film was measured for both wavelengths, and for both reflection and transmission (except films to thick for transmission). The three optical constants were then plotted as functions of time on the following pages.
SILVER-AIR TRANSMISSIVITY

GRAPH 2

TRANSMISSIVITY

TIME IN MINUTES

VACUUM
AIR

SUB. 2 4047 A
SUB. 2 4358 A
SUB. 3 4047 A
SUB. 3 4358 A
SUB. 1 4047 A
SUB. 1 4358 A
SUB. 13 4047 A
SUB. 13 4358 A
SILVER-AIR REFLECTIVITY

GRAPH 3.

TIME IN MINUTES

VACUUM AIR
PLEASE NOTE:
ON THIS & FOLLOWING GRAPHS
S = SUBSTRATE
A = 4047 Å
B = 4358 Å

SILVER - AIR ABSORPTIVITY
GRAPH 4

TIME IN MINUTES
COPPER-AIR TRANSMISSIVITY

GRAPH 5

TIME IN MINUTES
COPPER-AIR REFLECTIVITY

GRAPH 6

TIME IN MINUTES

0 1 5 10 15 20

TEST 6-B
S-6-A
S-5-B
S-5-A
S-2-B
S-2-A

R

0.600

0.400

0.200

VACUUM

AIR
COPPER-AIR ABSORPTIVITY

GRAPH 7

TIME IN MINUTES

S-5-B
S-6-A
S-6-B
S-2-B
S-2-A
S-3-B
S-3-A

VACUUM
AIR

A

.500

.400

.300

.200

0 1 5 10 15 20

67
SILVER-NITROGEN TRANSMISSIVITY

GRAPH 8

TIME IN MINUTES
SILVER - NITROGEN REFLECTIVITY

GRAPH 9

TIME IN MINUTES
COPPER-NITROGEN TRANSMISSIVITY

GRAPH II

TIME IN MINUTES
COPPER - NITROGEN REFLECTIVITY

GRAPH 12

TIME IN MINUTES

R

0.500

S-8-B

S-8-A

S-9-B

S-9-A

S-7-A

S-7-B

S-10-B

S-10-A

VACUUM

NITROGEN
COPPER- NITROGEN ABSORPTIVITY

GRAPH 13
SILVER - ARGON TRANSMISSIVITY
GRAPH-14

TIME IN MINUTES

S - 18 - A
S - 18 - B
S - 17 - A
S - 17 - B
S - 16 - A
S - 16 - B

T
SILVER-ARGON REFLECTIVITY

GRAPH 15
SILVER-ARGON ABSORPTIVITY
GRAPH 16

TIME IN MINUTES

VACUUM ARGON

A

0.300

0.200

0.100

0.000

0 1 5 10 15 20

S-15-A

S-15-B

S-16-A

S-16-B

S-17-A

S-17-B
COPPER-ARGON TRANSMISSIVITY
GRAPH 17

TIME IN MINUTES

0 1 5 10 15 20

VACUUM ARGON

S-2-A
S-2-B
S-20-A
S-20-B
S-1-A
S-1-B
S-19-A
S-19-B
COPPER-ARGON REFLECTIVITY

GRAPH 18

TIME IN MINUTES
COPPER-ARGON ABSORPTIVITY

GRAPH 19

TIME IN MINUTES

VACUUM

ARGON
SILVER-OXYGEN TRANSMISSIVITY
GRAPH 20
COPPER-OXYGEN TRANSMISSIVITY

GRAPH 23

TIME IN MINUTES

VACUUM OXYGEN
COPPER-OXYGEN REFLECTIVITY
GRAPH 24

TIME IN MINUTES
COPPER-OXYGEN ABSORPTIVITY

GRAPH 25

TIME IN MINUTES
Discussion of Results

X. The Changes in Optical Properties. The curves shown in Graph 2 through Graph 25 indicate the effects of various gases on the metallic films. In general the reflectivity of the films decreased when a gas was admitted to the chamber, the transmissivity increased, and the absorptivity decreased for highly reflecting films, and increased for highly transmitting films. Since absorptivity varied for all gases and films, this property could not be used to any significance in determining what occurred at the surface of the film when a gas was admitted to the chamber. For this reason the absorptivity will not be discussed in the following evaluation of the experiment.

A. Silver Vacuum-to-Air Optical Changes. Graph 2 of the transmissivity shows two major changes occurring. First, an initial change within the first 30 seconds which is quite abrupt in nature. This change was of the order of magnitude of 3-1/2 per cent. Second, a constant rate of change was also approximately 3-1/2 per cent. Graph 3 shows the reflectivity as a function of time. Generally it is made up of only one change, this being a decrease of two or three per cent, taking place in the first minute after the admission of air.
B. Copper Vacuum-to-Air Optical Changes. Graph 5 relates the transmissivity to time. The change here is similar to silver except the initial change takes place in a period longer than that required for silver. The period of this initial change is about two minutes. The per cent change of copper in the initial period is seven to nine per cent. The constant rate of change noted for the transmissivity is three to four per cent. The reflectivity in Graph 6 of the copper films differs from silver vacuum-to-air films in that it is also made up of two changes. An initial change occurring in the first two minutes and a second constant rate of change. The initial change was around seven per cent and the constant rate of change was about eight per cent over a period of 21 minutes.

C. Silver Vacuum-to-Nitrogen Optical Changes. Graph 8 shows the transmissivity of these films. For films of high transmission there is an initial increase of about two per cent occurring in the first 30 seconds and a gradual increase of about three per cent over 21 minutes. The films of low transmission show no initial change but do show a gradual change of six per cent increase over the 23 minute period. The film on substrate 12 Graph 9 indicates that the reflectivity increases four per cent over the 23 minute period. Some show an initial change and then a gradual decrease in reflectivity, while others just decrease at a constant rate.
D. Copper Vacuum-to-Nitrogen Optical Changes. Films of high transmissivity (Graph 11) behave as the copper films in the copper vacuum-to-air curves. The films of low transmission do not have such a sharp initial change. Total change over the 23 minute period is around 12 per cent for the high transmission films and ten per cent for the low transmission films, both changes representing an increase. Reflectivity in Graph 12 for these films is almost identical to the copper vacuum-to-air films, except the initial change is approximately eight per cent and the gradual change around 12 per cent.

E. Silver Vacuum-to-Argon Optical Changes. Graphs 14 and 15 show the transmissivity and reflectivity, respectively, of the silver vacuum-to-argon optical changes. The transmissivity in general does not show a sharp initial change, although there is an initial change on the film deposited on substrate 17. However, there is a gradual change over the 23 minute period representing an increase of about three per cent on the average. The reflectivity, with the exception of substrate 15 (4358 A), does not show an initial decrease but only a gradual decrease of several per cent.

F. Copper Vacuum-to-Argon Optical Changes. Again transmission shows an initial change for the high transmission films of the order of two per cent increase, and a gradual change of six per cent increase over a 21 minute period. The reflectivity as shown in Graph 18 indicates no initial change but a decrease
of two or three per cent over the 23 minute period.

G. Silver Vacuum-to-Oxygen Optical Changes. In general the transmission (Graph 20) shows an initial increase in the first two minutes and then a gradual increase over the duration of measurements. The initial increase is around six per cent and the gradual increase over 21 minutes is around seven per cent. The reflectivity (Graph 21) made only one change, this being an initial decrease of about 3-1/2 per cent in the first 12 seconds.

H. Copper Vacuum-to-Oxygen Optical Changes. Oxygen changed the transmissivity (Graph 23) approximately eight to ten per cent in the first 12 seconds after the admission of the oxygen, and then the transmissivity seemed to level off and increased in general only 1/2 of one per cent over the 22 minute period. Graph 24 shows that the reflectivity decreased by as much as 12 per cent in the first minute and further decreases did not exceed two per cent (most of the films remained at a constant reflectivity after the initial change).

II. Table of Results. For convenience a table has been prepared to indicate the effects of the gases on the films of silver and copper. The results shown here are general in nature and should be used only when concerned with generalities. The initial and gradual columns under transmissivity and reflectivity in Table 10 refer to the approximate percentage change of the initial change of the film upon exposure to the given gas.
Table 10 - Table of Results

<table>
<thead>
<tr>
<th>Gas</th>
<th>Transmissivity</th>
<th>Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Gradual</td>
</tr>
<tr>
<td>Air</td>
<td>3½%</td>
<td>3½%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Argon</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>3½</td>
<td>-</td>
</tr>
</tbody>
</table>

Copper

<table>
<thead>
<tr>
<th>Gas</th>
<th>Transmissivity</th>
<th>Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Gradual</td>
</tr>
<tr>
<td>Air</td>
<td>7-9%</td>
<td>3½%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Argon</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8½</td>
<td>7½</td>
</tr>
</tbody>
</table>

III. Interpretation of Results. If Table 10 is investigated it is immediately seen that oxygen brought about definite changes in the properties of transmission and reflection. It is also seen that nitrogen brought about considerable change and cannot be neglected. Argon also caused slight changes in these optical properties. The problem then seems to consist of several factors, each of which contributes to the change of transmissivity and reflectivity of silver and copper films when exposed to air.
It is known that oxygen would cause copper or silver to oxidize at room temperature (34), and this could cause the changes noted on the silver and copper films when exposed to oxygen. However, nitrogen must be considered further.

A. Chemisorption. When strong affinities exist between the solid and the environment, adsorption, if it occurs at all, is called chemisorption, indicative of strong bonding. Subsequent layers of adsorbate on chemisorbed layers are much less tightly held because surface forces are so effectively diminished by the first layer and, hence, the bonding tends toward the weaker so-called physical adsorption (32). It is quite difficult to draw a line between chemisorption and physical adsorption.

Forces at the surface of a metallic film are extensions of those forces which lie under the surface in the metallic medium. Since at the surface of a metal film or bulk metal the average number of neighbors of surface atoms is only half as many as the atoms below the surface, unbalanced forces occur at the surface. It is for this reason that some surfaces have a marked affinity for its environment, and also display stronger bonding of surface atoms of their underlying neighbors and to themselves than is common to the underlying metal atoms. Several facts are well known in regard to these surfaces forces. The strength of bonds between atoms increases as the number of neighbors decrease (27). As the strength of bonds increases, atoms move closer to each other, or the interatomic distance decreases (32). From
this is indicated that the distance between surface atoms with
stronger-than-usual bonding to each other is less than the
interatomic spacing found under the surface. If this is so
there is a tendency of the atoms to compress atoms underneath,
giving rise to the familiar surface tension easily demonstrated
by liquids but difficult to show on metals. In view of the
way in which Adam (1) has pictured oxygen chemisorbed on
tungsten and carbon monoxide chemisorbed on platinum, it is
feasible to picture the chemisorption of nitrogen on silver
or copper as shown in Figure 16. In this figure the nitrogen
bond has been broken and electrons are shared with the silver
(or copper as the case may be since they have the same valance).

B. Physical Adsorption. The most obvious distinction between
physical adsorption and chemisorption is the head of adsorption.
For physical adsorption the heat of adsorption is usually less
than 4000 calories per mole, while chemisorption is higher,
generally at least 10,000, and occasionally up to 200,000
calories per mole (2). In physical adsorption the gas may be
easily pumped off, particularly if the temperature is raised
slightly. But nevertheless it is difficult to tell the point
separating physical adsorption and chemisorption.

C. Effect of Sorption on Changes of Optical Properties of
Metallic Films. Argon is an inert gas and would not be
chemisorbed at room temperatures. Argon could, however, be
physically adsorbed. If the curves where argon was used were
Figure 16
Chemisorption of nitrogen on silver

Figure 17
Exaggerated transmission of films in nitrogen

Figure 18
Exaggerated reflection of films in nitrogen
studied it is seen that they display no initial change, only a gradual change. This gradual change is thought to be caused by physical adsorption. Nitrogen does cause a slight initial change in the optical properties of silver, and an even greater change with copper. Nitrogen also caused a gradual increase in transmissivity and decrease in reflectivity. Applying the knowledge learned from argon it is indicated that physical adsorption caused the gradual change, and it is then indicated that chemisorption caused the initial change. Figure 16 shows a monatomic layer of nitrogen chemisorbed on a silver film, while Figures 17 and 18 diagram the regions of chemisorption and physical adsorption of films exposed to nitrogen. It is not likely that external pressure on the surface of the metallic films produced optical changes, because pressure should cause immediate changes since the pressure was brought from approximately $5 \times 10^{-4}$ mm of Hg to atmospheric pressure in 10 seconds or less. If pressure affected the optical properties, it therefore should have been immediate and would have displayed this change on all films regardless of the gas. Argon did not display such a change, and hence pressure did not affect the optical properties in a detectable manner.

IV. Evaluation of the Interpretation. The changes in optical properties when metallic films are exposed to air can be contributed to a combination of oxidation and sorption. Since the atmosphere is made up primarily of nitrogen and oxygen in
the ratio of 4 to 1, respectively, then if the changes noted by this experiment for pure oxygen or nitrogen are multiplied by their relative concentration in the atmosphere, and these products added, the results should compare favorably with the measurements obtained for air. Table 11 shows such a comparison. All values in this table are approximate. Agreement between the predicted and the measured values in the air is fair.

The gradual change in the reflectivity of silver and copper films seems to be caused almost entirely by nitrogen as noted in the table.

### Table 11 - Comparison of Optical Property Changes With Measured Changes in Air

<table>
<thead>
<tr>
<th></th>
<th>Silver Transmissivity</th>
<th>Silver Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Gradual</td>
</tr>
<tr>
<td>Partial Change Due to Nitrogen</td>
<td>1.6 %</td>
<td>2.4 %</td>
</tr>
<tr>
<td>Partial Change Due to Oxygen</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Total Change</td>
<td>2.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Measured Changes in Air</td>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 11 (continued)

<table>
<thead>
<tr>
<th>Copper</th>
<th>Transmissivity</th>
<th>Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Gradual</td>
</tr>
<tr>
<td>Partial Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Due to Nitrogen</td>
<td>4 %</td>
<td>5.6 %</td>
</tr>
<tr>
<td>Partial Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Due to Oxygen</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Total Change</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Measured Changes in Air</td>
<td>8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

V. Agreement with Previous Interpretations. The changes noted in working with air in this experiment are in agreement with other observations (17, 12). However, Edwards and Petersen (17) attributed the initial change in transmissivity and reflectivity of magnesium-aluminum films to the effects of pressure and oxidation, and this experiment indicated that it was not pressure dependent, but the changes were caused by chemisorption and oxidation. Cheo (12) has indicated that the transmissivity of silver films exposed to air decreases with time, but the transmissivity of silver in all cases in this experiment was found to increase upon exposure to air and the various other gases.

VI. Irregularities in Transmission, Reflection and Absorption Curves. Severe irregularities are noted in several of the transmission and reflection curves, and in a larger number of absorption curves. No definite reason could be given as to
the origin of these deviations from the general trend. However, contamination or unsteadiness of the mercury arc source could introduce such effects.

VII. Suggestions for Further Study. To more conclusively show that chemisorption and physical adsorption are partially responsible in bringing about changes noted in this experiment, it is suggested that the following investigations be made.

A. Cooling the Metallic Film. If the metallic film in question were cooled by liquid air, or some other means of reaching a low temperature, before gas was admitted to the chamber, then it would be possible to see if physical adsorption brought about the secondary or gradual change as noted in this experiment. This is based on the fact that since the film would be cooler, gases would more readily condense on the film surface. If this were the case, then the slope of the secondary or gradual change as noted in this work would be increased.

B. Outgassing the Metallic Film. By use of a high-speed vacuum system and by slightly heating the metallic film, the metallic film could be outgassed. The outgassing should remove only the physically adsorbed gas from the surface and, hence, during outgassing the transmissivity would be expected to decrease and the reflectivity increase.

VIII. Another Interpretation of the Results. As the optical properties in oxygen behave in the same general way as in nitrogen, that is with an abrupt initial change, it could be
said that chemisorption brought about the initial change in oxygen just as it did in nitrogen. Atoms like oxygen, nitrogen, and hydrogen which have either available bonding orbitals or electrons, will be chemisorbed (35). Thus, oxygen should be chemisorbed as readily on silver and copper as nitrogen, and oxygen has already been proven to be chemisorbed on such metals as tungsten (1). Hence, the question arises as to whether oxygen oxidizes the metallic surface, or whether oxygen is chemisorbed on the surface of the metal. There is no way possible to distinguish between the two effects from the observations made in this experiment.
Conclusion

The changes in the transmissivity, reflectivity, and absorptivity of evaporated metal films due to exposure of several gases revealed that:

1. These properties do change when air is admitted to the vacuum where the films were freshly prepared.

2. The transmissivity in air consistently increased for silver and copper, the greater change occurring with copper.

3. The reflectivity in air consistently decreased for both silver and copper, the greater change occurring with copper.

4. Two changes were prominent when air was used. An initial change followed by a gradual change in the properties of transmission and reflection.

5. Nitrogen and oxygen produced similar changes, but of different magnitudes, as was produced by air.

6. Argon, when admitted to the vacuum chamber, produced a very slight initial change followed by a gradual change in the transmissivity and reflectivity.

7. The initial change caused by oxygen was attributed to oxidation and the initial change in nitrogen was caused by chemisorption.

8. The gradual change, when it occurred, was attributed to physical adsorption.
9. The possibility existed that chemisorption also caused the initial change in oxygen, but in this experiment no definite conclusion could be reached.
The reflectivity, transmissivity, and absorptivity of freshly evaporated silver and copper films were measured in vacuo and then in the presence of several gases. These measurements were performed, using the photoelectric method, with two photomultiplier tubes (931-A and 1P21), and were made at an angle of incidence of zero degrees for two different wavelengths (4047 Å and 4358 Å).

The gases used were air, argon, nitrogen and oxygen. The use of oxygen required several changes in the evaporating system in order that the diffusion pump oil would not oxidize to rapidly and cause an explosion.

Air was found to increase the transmissivity in two steps, first an initial change, and second a gradual change. The reflectivity decreased in two similar changes.

Nitrogen and oxygen revealed to a greater or lesser extent the same changes as were observed for air. Argon produced only a gradual change in both reflectivity and transmissivity.

The initial change in oxygen was attributed to oxidation, and the initial change in nitrogen attributed to chemisorption. The gradual change in all gases was due to physical adsorption.

The possibility that chemisorption might have caused the initial change in oxygen was pointed out, but this experiment did not allow a definite choice to be made.
Acknowledgements

The author would like to express his sincere appreciation to all those who have helped in this work. He especially wishes to thank Dr. H. Y. Loh for the benefit of his forethought and encouragement in carrying out this experiment. His gratitude is expressed to Dr. T. Leinhart for fruitful discussions in regard to the vacuum system, and for the liquid air provided by his laboratory. He is grateful to Dr. T. M. Hahn for making available the recording potentiometer which greatly improved the experiment.

He is also deeply grateful to his wife for her help in reading and plotting the many points involved in this work, and for her care in typing this manuscript. He wishes to thank his parents for making the completion of this work possible.
Bibliography

Literature Cited


2. ibid., p. 252.


5. ibid., p. 68.

6. ibid., p. 69.

7. ibid., p. 13.

8. ibid., p. 16.

9. ibid., p. 17.

10. ibid., p. 37.

11. ibid., p. 33.

12. ibid., p. 52.


35. ibid., p. 225.
Bibliography

Literature Reviewed


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Glossary

Absorptivity - The ratio of the intensity of the light absorbed to the intensity of the incident light of a particular wavelength.

Chemisorption - When strong affinities exist between the solid and the environment, adsorption, if it occurs at all, is called chemisorption, indicative of strong bonding.

Coefficient of Absorption - See absorptivity.

Coefficient of Reflection - See reflectivity.

Coefficient of Transmission - See transmissivity.

Extinction Coefficient - The index of refraction of metals is always a complex quantity. The extinction coefficient is the imaginary part of the complex index of refraction.

Index of Refraction - The ratio of the velocity of light in vacuo to the velocity of light in a given medium.

Optical Constants - The five quantities, reflectivity, transmissivity, absorptivity, index of refraction and extinction coefficient, are known as the optical constants.

Physical Adsorption - Subsequent layers of adsorbate on chemisorbed layers are much less tightly held because surface forces are so effectively diminished by the first layer and, hence, the bonding tends toward the weaker so-called physical adsorption.
Reflectivity - The ratio of the intensity of the light reflected to the intensity of the incident light of a particular wavelength.

Substrate - The underlying layer upon which films are formed.

Transmissivity - The ratio of the intensity of the light transmitted to the intensity of the incident light of a particular wavelength.
ABSTRACT

The reflectivity, transmissivity, and absorptivity of freshly evaporated silver and copper films were measured in vacuo and then in the presence of several gases. These measurements were performed, using the photoelectric method, with two photomultiplier tubes (931-A and 1P21), and were made at an angle of incidence of zero degrees for two different wavelengths (4047 A and 4358 A).

The gases used were air, argon, nitrogen and oxygen. The use of oxygen required several changes in the evaporating system in order that the diffusion pump oil would not oxidize to rapidly and cause an explosion.

Air was found to increase the transmissivity in two steps, first an initial change, and second a gradual change. The reflectivity decreased in two similar changes.

Nitrogen and oxygen revealed to a greater or lesser extent the same changes as were observed for air. Argon produced only a gradual change in both reflectivity and transmissivity.

The initial change in oxygen was attributed to oxidation, and the initial change in nitrogen attributed to chemisorption. The gradual change in all gases was due to physical adsorption.

The possibility that chemisorption might have caused the initial change in oxygen was pointed out, but this experiment did not allow a definite choice to be made.