Best Available Copy

LOAN DOCUMENT

AD-A283 100

DTIC ACCESSION NUMBER

LEVEL

O

INVENTORY

Rept 1180

DOCUMENT IDENTIFICATION

7 Sept 1950

DISTRIBUTION STATEMENT

ACCESSION FOR		
NTIS	GRAAI	☑
DTIC	TRAC	☐
UNANNOUNCED		☐
JUSTIFICATION		

BY

DISTRIBUTION/

AVAILABILITY CODES

DISTRIBUTION	AVAILABILITY AND/OR SPECIAL

A-1

DISTRIBUTION STAMP

**DTIC
ELECTE
AUG 1 8 1994
S
G
D**

DATE ACCESSIONED

DATE RETURNED

**H
A
N
D
L
E**

**W
I
T
H**

**C
A
R
E**

94 7 27 022

DATE RECEIVED IN DTIC

94-23872

REGISTERED OR CERTIFIED NUMBER

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-FDAC

ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES

AD A 283 100

Report 1180

PROPERTIES, OXIDATION, DECOMPOSITION, AND

APPLICATIONS OF THIN FILMS OF SILICON MONOXIDE

Project 8-23-02-002

7 September 1950

Submitted to

THE CHIEF OF ENGINEERS, U. S. Army

by

The Commanding Officer
Engineer Research and Development Laboratories

Prepared by

Dr. Georg Hass
Radiation Branch
Engineer Research and Development Laboratories
Fort Belvoir, Virginia

TABLE OF CONTENTS

Foreword

The material here presented is the result of work carried on by Dr. Georg Hass of the Radiation Branch, Engineer Research and Development Laboratories, Fort Belvoir, Virginia, from July 1949 to April 1950. A resume of this report was presented at the annual meeting of the American Ceramic Society, on 26 April 1950, at New York City, New York.

ABSTRACT

A material satisfying the chemical formula for silicon mon-
oxide can be made by controlled condensation of vapors obtained by
heating finely divided silicon and silica in vacuum. Silicon mon-
oxide is structurally different from either silicon or silicon
dioxide, and exists only in amorphous form. The relatively low
temperature at which silicon monoxide evaporates, its amorphous
structure, and the good chemical and mechanical resistance of thin
films of this material make it especially suitable for producing
protective layers on front-surface mirrors and for preparing replica
and support films for electron microscope and electron diffraction
studies. Unlike silicon dioxide, silicon monoxide absorbs strongly
in the ultraviolet. The increase in ultraviolet transmission of
silicon monoxide films in air at various temperatures has been
used to measure their oxidation to silicon dioxide. Slow de-
posited films of silicon monoxide oxidize more rapidly and deeper
than fast deposited ones. The looser structure and lower density
of slow condensed films accounts for this difference in oxidation
behavior. When a vacuum-deposited thin film of silicon monoxide is
heated in an inert atmosphere, it remains unchanged up to tempera-
tures of about 600 C, but it decomposes to silicon and silica when
exposed to higher temperatures for several hours. The heat-treated
decomposed film has higher absorption in the visible and ultra-
violet than has the untreated silicon monoxide coating. On heating
to between 850 and 900 C in a vacuum of an oil diffusion pump the
precipitated silicon of the decomposed films of silicon monoxide
is changed to silicon carbide. The cracking of oil molecules on
heated surfaces furnishes the carbon for this reaction. Methods
for preparing replica and support films of silicon monoxide and
their various uses for electron microscope and electron diffrac-
tion studies are described.

1

PROPERTIES, OXIDATION, DECOMPOSITION, AND
APPLICATIONS OF THIN FILMS OF SILICON MONOXIDE

I. INTRODUCTION

The generally known oxide of silicon is silicon dioxide, which exists in various modifications. However, under special conditions a lower oxide of silicon, silicon monoxide, can also be formed. The existence of silicon monoxide was first reported by Potter[1] in 1907. More recent investigations on the preparation, behavior, and absorption spectra of this compound have been published by Bonhoeffer,[2] Biltz and Ehrlich,[3] Zintl and others,[4] Gel'd and Kochnev,[5] Grube and Speidel,[6] and Erasmus and Persson.[7] An extensive review of the literature concerning silicon monoxide and its bearing on steel practice has been reported by Zapffe and Sims.[8]

One of the attractive properties of silicon monoxide is its relatively high vapor pressure. It evaporates at much lower temperature than silicon or silicon dioxide, and condenses on cooler surfaces in uniform and adherent films when evaporated in high vacuum. Silicon monoxide is, therefore, especially suitable for producing protective layers on front-surface mirrors,[9] and for preparing replica and support films for electron microscope and electron diffraction studies.[10] It can also be applied as a thin inter-layer to increase the adherence of metallic coatings on glass, plastic, and metals.[11]

In spite of the extensive literature published on silicon monoxide, very little is known in regard to the oxidation rates of silicone monoxide in air at various temperatures, its decomposition at high temperatures, and the effect of the speed of evaporation on

1. H. N. Potter, Trans. Am. Electrochem. Soc. 12, 191 (1907).
2. K. F. Bonhoeffer, Zs. F. phys. Chem. 131, 363 (1928).
3. W. Biltz and P. Ehrlich, Naturwiss 26, 188 (1938).
4. E. Zintl, W. Brauning, H. Grube, W. Krings, and W. Morawietz, Zs. f. anorg. allgem. Chem. 245, 1 (1940).
5. P. V. Gel'd and M. I. Kochnev, Doklady Akad, Nauk, S.S.S.R. 61, 649 (1948), and Zhur Priklad Khim 21, 1249 (1948).
6. G. Grube and H. Speidel, FIAT Review of German Science 1939-1946, Inorganic Chemistry, Part I, pp. 263-4 (1948).
7. H. deWet Erasmus and J. A. Persson, J. Electrochem. Soc. 95, 316 (1949).
8. C. A. Zapffe and C. E. Sims, Iron Age, 149, No. 4, pp. 29-31 (Jan 22, 1942) and No. 5, pp. 34-39 (Jan 29, 1942).
9. G. Hass, German Patent DRP. Nr. 280/42 (1942), and G. Hass and N. W. Scott, J. Opt. Soc, Am. 39, 179 (1949).
10. G. Hass and H. Kehler, Optik 5, 48 (1949).
11. G. Hass, German Patent DRP. Nr. 208/43 (1943).

the condensate formed.

The present paper presents data on these reactions and phenomena, which have a great influence on the properties and behavior of vacuum-deposited silicon monoxide films and discusses the application of these films for electron microscope and electron diffraction studies.

II. PREPARATION, DENSITY, AND STRUCTURE OF SILICON MONOXIDE FILMS

Some of the reactions which produce silicon monoxide at relatively low temperature are as follows:

(1) $SiO_2 + Si \rightarrow 2 SiO$

(2) $SiO_2 + H_2 \rightarrow SiO + H_2O$

(3) $SiO_2 + C \rightarrow SiO + CO$

(4) $Si + MeO \rightarrow Me + SiO$

(5) $Al_2O_3.2SiO_2 + 2Si \rightarrow Al_2O_3 + 4SiO$

The first reaction is most suitable for producing large quantities of silicon monoxide and for preparing thin films of this material. The mixture of silicon and silicon dioxide begins to give off noticeable amounts of silicon monoxide vapor at about 1100 C. It can, therefore, be used directly for depositing thin films of silicon monoxide. However, more consistent results are obtained by using as starting material a silicon monoxide condensate prepared by reaction (1). Reaction (2) gives the partial reduction of silicon dioxide by hydrogen. It also starts to become noticeable at about 1100 C, and is of interest for the silica glass industry since this reaction can decrease remarkably the ultraviolet transmission of silica glass. Reactions (3) and (4) demonstrate that silicon monoxide films can also be deposited by heating silica in a carbon crucible or silicon in a container of high melting oxides. Reaction (5) shows that not only free silica but also silica bound in silicates can be reduced with suitable reducing agents and removed at high temperatures. The reaction can be used for desilicification of silicates if the desilicified materials have lower volatility than silicon monoxide.

Fig. 1 shows a sketch of the arrangement used for producing silicon monoxide by heating silicon and silica in vacuum. It demonstrates the influence of the temperature on the condensate formed. A mixture of finely divided silicon and silica is placed
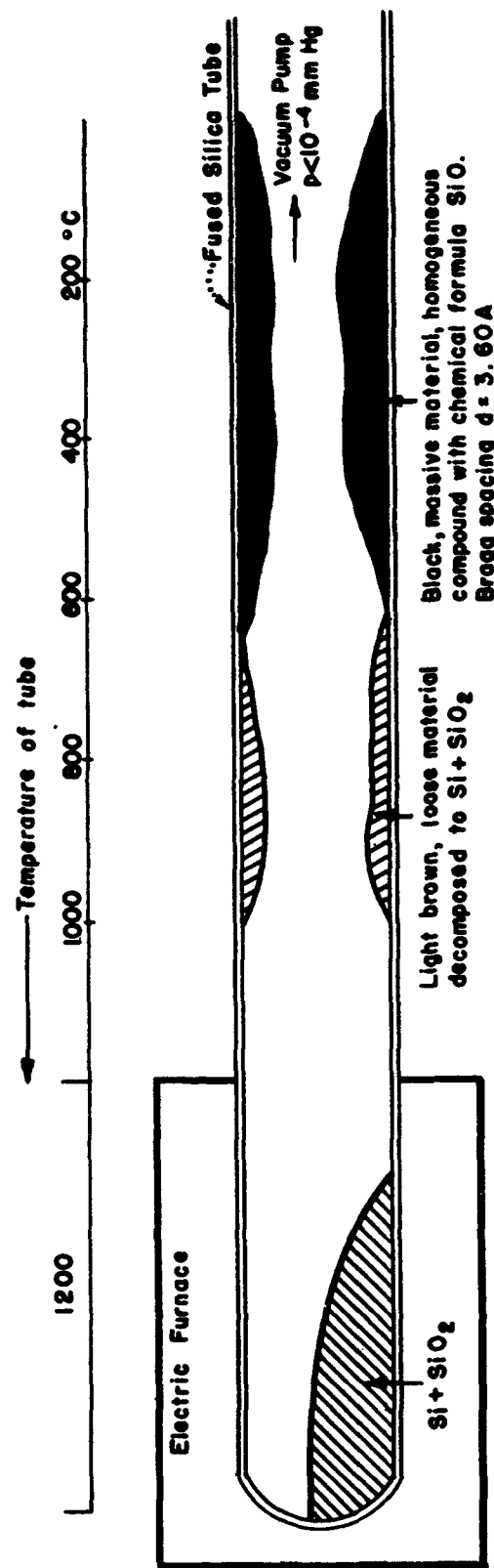
Fig. 1. Arrangement for producing SiO.

in the closed end of a silica tube. The tube is inserted horizontally in a furnace, evacuated to a pressure lower than 10^{-4} mm Hg and heated to about 1250 C. Silicon monoxide evolves from the heated mixture and condenses on the cooler parts of the silica tube. The upper scale shows the temperature distribution along the silica tube during the evaporation and recondensation of silicon monoxide. The silicon monoxide vapor condensed at a temperature higher than 800 C forms a loose, light brown material, while the condensate obtained at lower temperatures is dark brown to black, massive and glasslike. There is always much more material condensed at the low temperature side of the silica tube than at the high temperature one, indicating that the silicon monoxide that condenses at a temperature of 800 C or higher re-evaporates to a high degree. Both types of condensed material have been investigated with monochromatic X-rays. The light brown material shows sharp lines of silicon and diffuse rings of silica and is, therefore, a mixture of crystalline silicon and amorphous silica. That means that silicon monoxide vapor becomes decomposed to silicon and silica if it is condensed at high temperatures. The X-ray diffraction pattern of the dark material has neither a diffraction ring of silicon nor of silica. It shows with appreciable intensity only one halo, corresponding to a Bragg spacing of about 3.60 A. The dark condensate is a homogeneous, amorphous material satisfying the chemical formula for silicon monoxide, a fact that can be demonstrated by a chemical test using hydrofluoric acid, in which it is found to be completely soluble, while the light brown condensate leached with hydrafluoric acid becomes dissolved only to approximately 68 percent, leaving insoluble finely divided silicon.

The apparatus for producing thin films of silicon monoxide by evaporation in high vacuum is shown in Fig. 2. The vacuum chamber is a glass bell jar, 17 inches in diameter and 27 inches high, placed on a metal base plate. The heating element for the silicon monoxide is mounted close to the base plate, and consists of a boat, made from a sheet of tantalum measuring 4 by 1.5 by 0.008 inches, filled with small pieces of silicon monoxide. The current to heat the boat, and thus its temperature and the speed of evaporation of the silicon monoxide, can easily be controlled and varied. The mirror form or substrate to be coated with silicon monoxide is placed in the upper part of the evaporation chamber 15 to 20 inches above the evaporation source. Before the evaporation is performed, the mirror form is cleaned by a high voltage glow discharge of 5000 volts at 75 milliamperes for 10 minutes to increase the adherence of vacuum-deposited films. The high voltage discharge electrode (cathode) consists of an aluminum ring placed midway between the mirror form and the evaporation elements. High reflecting coatings of aluminum can be deposited and protected with silicon monoxide in the same vacuum unit.
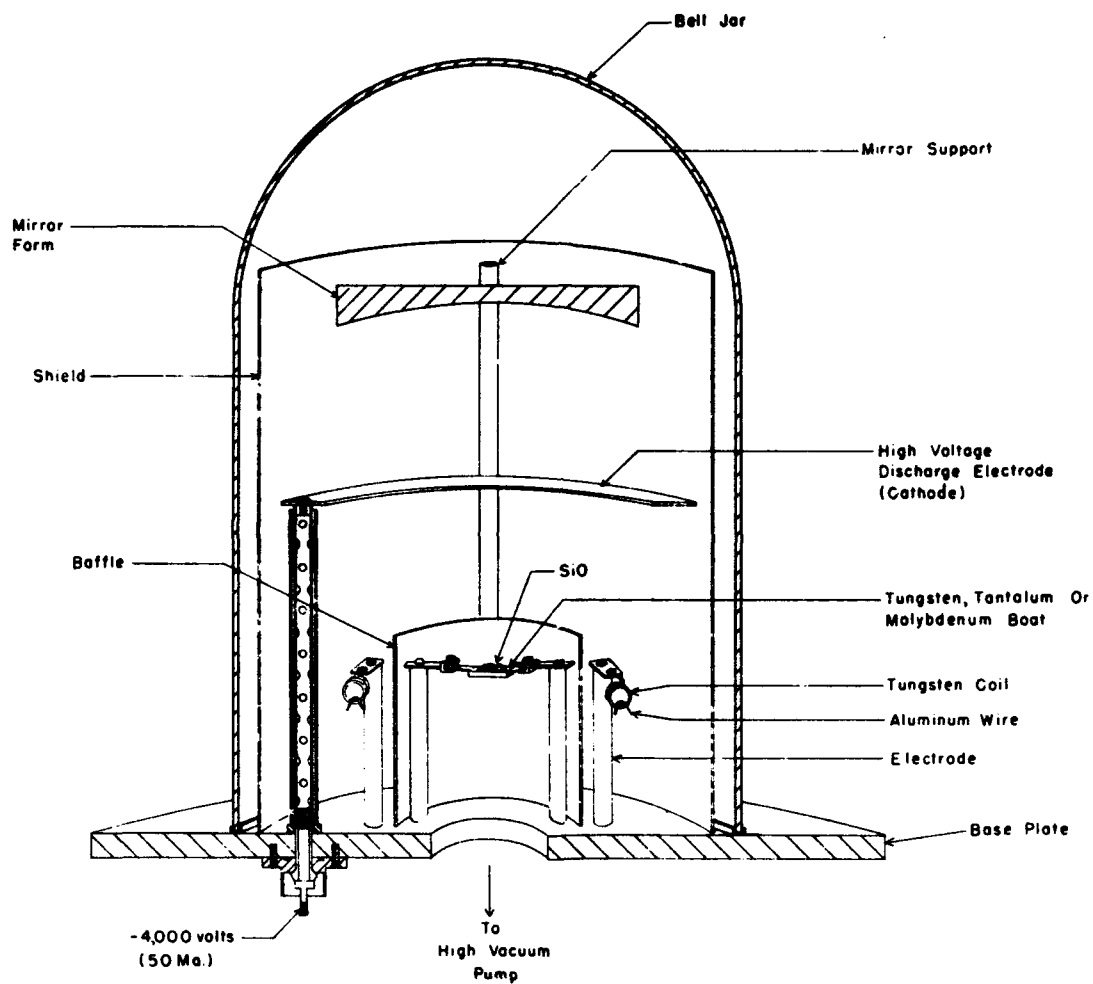
Bell Jar

Mirror Support

Mirror
Form

Shield

High Voltage
Discharge Electrode
(Cathode)

Baffle

SiO

Tungsten, Tantalum Or
Molybdenum Boat

Tungsten Coil

Aluminum Wire

Electrode

Base Plate

-4,000 volts
(50 Ma.)

To
High Vacuum
Pump

Fig. 2. Vacuum apparatus for preparing silicon monoxide films.

6

Fig. 3 shows the deposition rates in Angstrom units per second (Al sec) and the density of the films condensed as functions of the boat temperature. The true compound silicon monoxide with a density of 2.15 g per cu cm was used as starting material. All evaporations were carried out at a vacuum of about 1 to 2 x 10⁻⁵ mm Hg and the vapor was condensed 18 inches above the evaporation source. After the boat had reached a constant temperature, which was measured by platinum platinum-rhodium thermocouple, the silicon monoxide vapor was allowed to condense on an optically flat glass for 4 to 10 minutes. The amount of the condensate obtained was determined with a microbalance and its thickness was measured by means of Wiener's interference fringes greatly sharpened through a multiple beam action.[12] Thus the condensation rates and the density of the deposited material could be determined with high accuracy. The speed of evaporation increased rapidly with the temperature, as expected. The density of the films produced at a deposition rate of 6 to 12 A per second, or a boat temperature of 1200 to 1250 C, was about the same as that of the starting material. But it was higher for very rapidly condensed films and lower for slow condensed ones. If silicon monoxide is evaporated at higher pressure ($p > 10^{-4}$ mm Hg) the condensed films have lower densities than those shown in Fig. 3. The fact that coatings produced by slow evaporation or at higher pressure have lower density and looser structure than the compact material is known, and was therefore expected.[13] The higher density of films prepared extremely fast with high boat temperature, however, can only be explained by assuming that their composition is different from that of the starting material. Since their density is higher than that of silicon monoxide (ρ = 2.15 g per cu cm) and silica glass (ρ = 2.2g per cu cm) but lower than that of silicon (ρ = 2.40 g per cu cm) it must be accepted that films produced with extremely high boat temperature contain more silicon than silicon monoxide does. This assumption is supported by the results of electron diffraction studies and optical investigations.

Fig. 4 shows the electron diffraction pattern of a silicon monoxide film. The vacuum-deposited films are like the dark material, mentioned above, condensed at relatively low temperature. They consist of amorphous, homogeneous material and the patterns of such films show one halo. The Bragg spacing calculated from this halo is d = 3.65 ± 0.05 A for films prepared with a boat temperature of 1250 C and lower, which is in agreement with the X-ray value of silicon monoxide. Films produced by faster evaporation, however, show a diffuse ring with greater diameter corresponding to a smaller spacing. If the evaporation is carried out at a temperature

12. S. Tolansky, J. Sci. Instr. 22, 161 (1945).
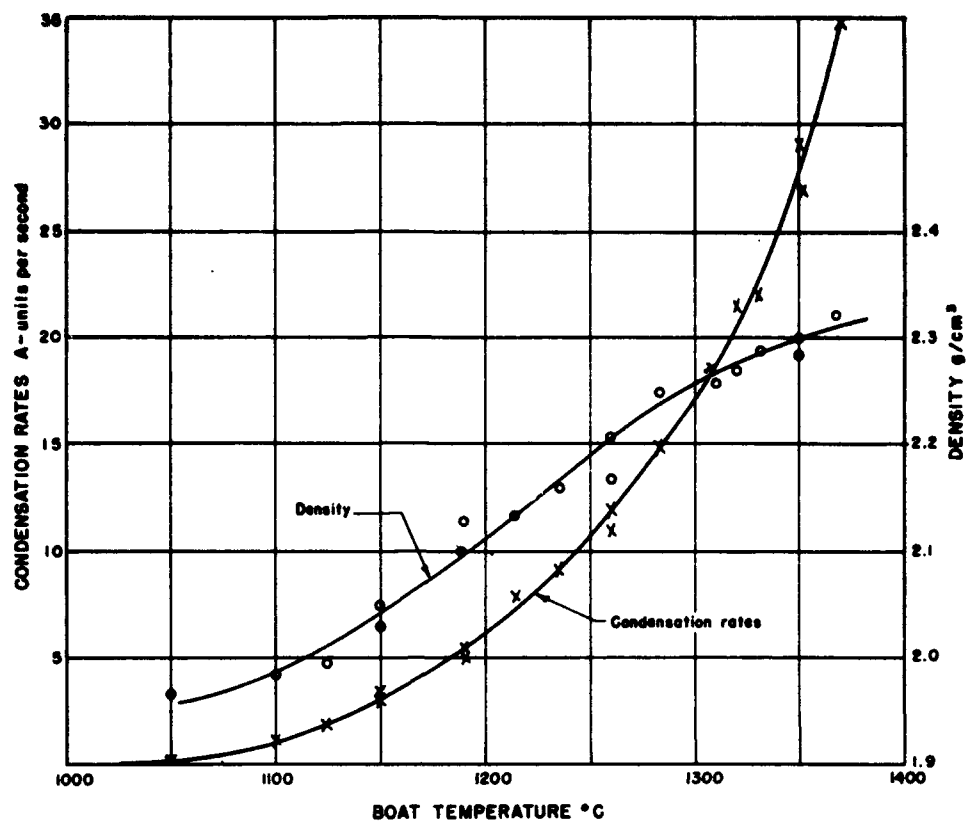13. W. Walkenhorst, Zs. Tech. Phys. 22, 14 (1941) and Dissertation Hannover (1940).

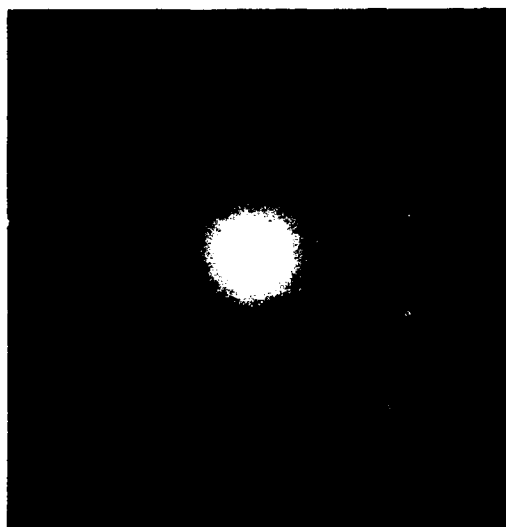Fig. 3. Rate of condensation and density of film deposited as functions of boat temperature.

Fig. 4. Electron diffraction pattern of a vacuum-deposited SiO film.

of about 1350 C the halo of the condensed film corresponds to
d = 3.45 ± 0.05 A. The halo of true silicon monoxide lies about
half way between the first strong ring of silicon (d = 3.15 A) and
that of silica (d = 4.10 A) but it becomes shifted closer to the
first silicon ring for material evaporated from highly heated boats.
Since the electron diffraction pattern of extremely fast evaporated
material shows only the intense halo and does not show either a
ring of silicon or silica, it must be assumed that a uniform solu-
tion of silicon and silica, having a silicon to oxygen ration of
greater than one, can exist.

III. OXIDATION OF SILICON MONOXIDE FILMS IN AIR AT VARIOUS TEMPERATURES

Thin films of silicon monoxide can be oxidized to silicon di-
oxide by heating them in air. Slow deposited films oxidize much
faster and at lower temperatures than the more compact, fast con-
densed ones. After the film is oxidized its diffraction pattern
has completely changed and shows with noticeable intensity seven
halos of amorphous silica. When the silica films are heated for
several hours at 950 to 1000 C they crystallize and show then a
sharp ring pattern which is identical with that of $\propto$-cristobalite.
The Bragg spacings (d-values) of the seven halos of silicon monoxide
film oxidized in air at 700 C compared with those obtained from
X-ray and electron diffraction patterns of amorphous silica by
Warren[14] and Koenig[15] are listed in Table I. The agreement is
rather good.

Table I. Bragg Spacings and Estimated Intensities of the Halos

		Bragg Spacing (d-values in Angstroms)		
		Electron Diffraction Pattern		X-ray Diffraction
Ring No.		ERDL	Koenig	Warren
1		4.10 (very strong)	4.1	4.17
2		2.40 (weak)	2.4	- - -
3		2.05 (very weak)	2.0	2.00
4		1.45 (very weak)	1.45	1.47
5		1.20 (strong)	1.18	1.25
6		0.97 (very weak)	0.96	0.98
7		0.80 (weak)	0.80	0.79

The exact oxidation rates of silicon monoxide films in air at
various temperatures can be determined by optical means. Unlike
silicon dioxide, silicon monoxide absorbs strongly in the ultraviolet.

14. R. E. Warren, J. App. Phys. 8, 645 (1937), and R. E. Warren and
J. Biscoe, J. Amer. Ceram. Soc. 21, 49 and 259, 1938.
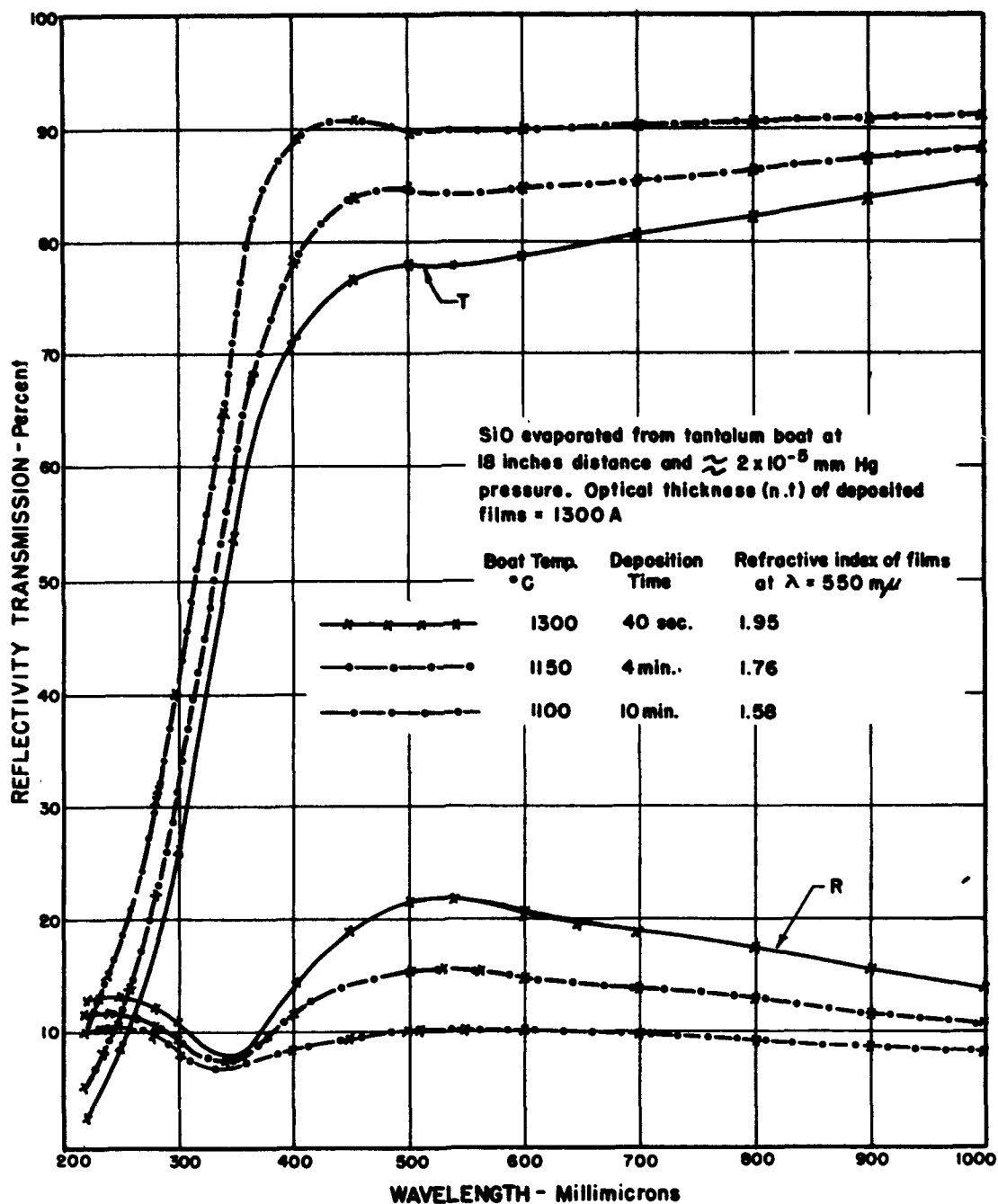15. H. Koenig, Optik 3, 419 (1948).

Fig. 5. Reflectivity and transmission of SiO films evaporated on SiO₂ plates at various speeds, as function of wavelength.

10

Thin films of silicon monoxide were evaporated onto ultraviolet trans-
parent silica plates and their ultraviolet absorption was measured
before and after exposure to air at various temperatures. The de-
crease of ultraviolet absorption was used to calculate the amount of
silicon monoxide oxidized to silica. Fig. 5 shows transmission and
reflection curves of fast and slow deposited silicon monoxide films.
All three films have an optical thickness of 1300 A. Their absorp-
tion in the visible and infrared region is very small but it is
high in the ultraviolet. The ultraviolet absorption and the re-
fractive index in the visible and infrared region increase with the
speed of evaporation. The increase in film density with speed of
evaporation is not sufficient to account for the large differences
in absorption coefficients and refractive indices. This can only
be explained by the fact that films resulting from fast evaporation
out of highly heated tantalum boats contain more silicon than is
present in true silicon monoxide.

The transmission and reflection curves shown in Fig. 5 were
measured in vacuum directly after the evaporation of silicon monoxide
took place. When the silicon monoxide films are exposed to air they
partially oxidize to silica. Thus, their absorbing thickness be-
comes less and their ultraviolet transmission increases. Fig. 6
compares the ultraviolet transmission of slow and fast evaporated
films before and after exposure to air at room temperature. Very
little change takes place in fast deposited films, but a strong
increase of transmission occurs in slow condensed ones. This dif-
ference in oxidation behavior is even more evident at higher tem-
peratures. Fig. 7 compares the ultraviolet transmission of slow and
fast deposited films before and after heat treatments at 400 C in
air and in air plus steam. The transmission of the slow condensed
film increases much more than that of the fast condensed one during
the heat treatment. The calculated oxidation rates of slow and
fast evaporated films are shown in Figs. 8 and 9. The thickness
of the silicon monoxide film which is oxidized to non-absorbing
silica can be calculated from the increase of ultraviolet trans-
mission by means of the third equation shown in Fig. 8. The ab-
sorption coefficient of the unoxidized material, α, can be deter-
mined by the first equation if the film thickness is measured.
$(t - t')$ is the thickness of silicon monoxide which is oxidized to
silica. $\frac{Io}{I_T}$ is the entering intensity divided by the transmitted
intensity before oxidation took place, and $\frac{Io}{I}$ the same after part
of the film is oxidized. After 5 days in air at room temperature,
460 A of the slow deposited and only 50 A of the fast deposited
silicon monoxide film are replaced by silicon dioxide. If the films
are heated in air their oxidation increases very rapidly. A slow
deposited silicon monoxide film of 800 A thickness can be com-
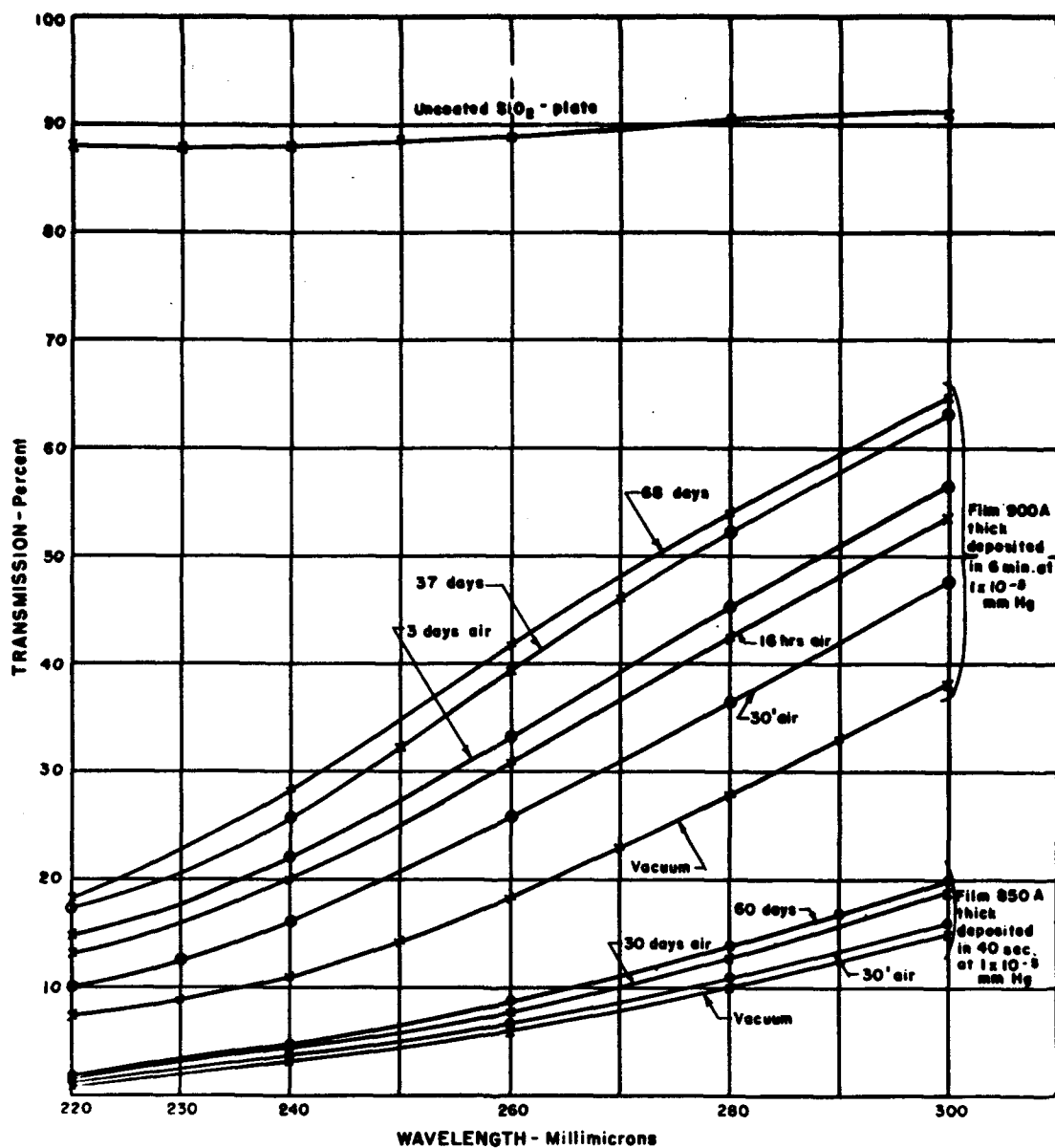pletely oxidized at 400 C in a few hours while the same treatment

Fig. 6. Increase of UV transmission of fast and slow deposited SiO films caused by oxidation in air at room temperature.
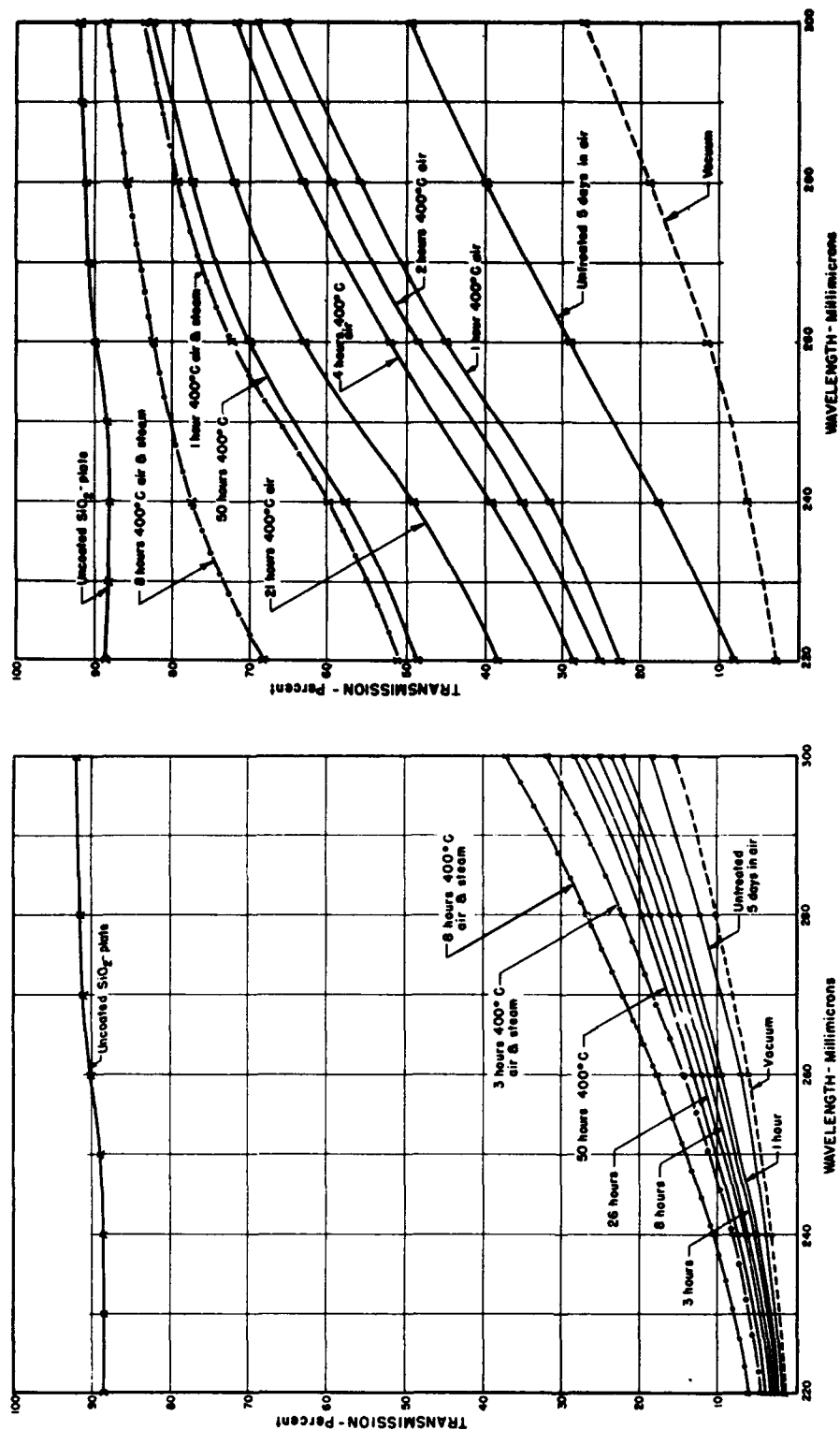
Fig. 7. Change of UV transmission of SiO films caused by oxidation at 400 C in air and in air and steam. Left: Fast deposited SiO film 850 A thick, deposited in 40 sec at 1 x 10⁻⁵ mm Hg. Right: Slow deposited film 1050 A thick, deposited in 9 min at 2 x 10⁻⁵ mm Hg.
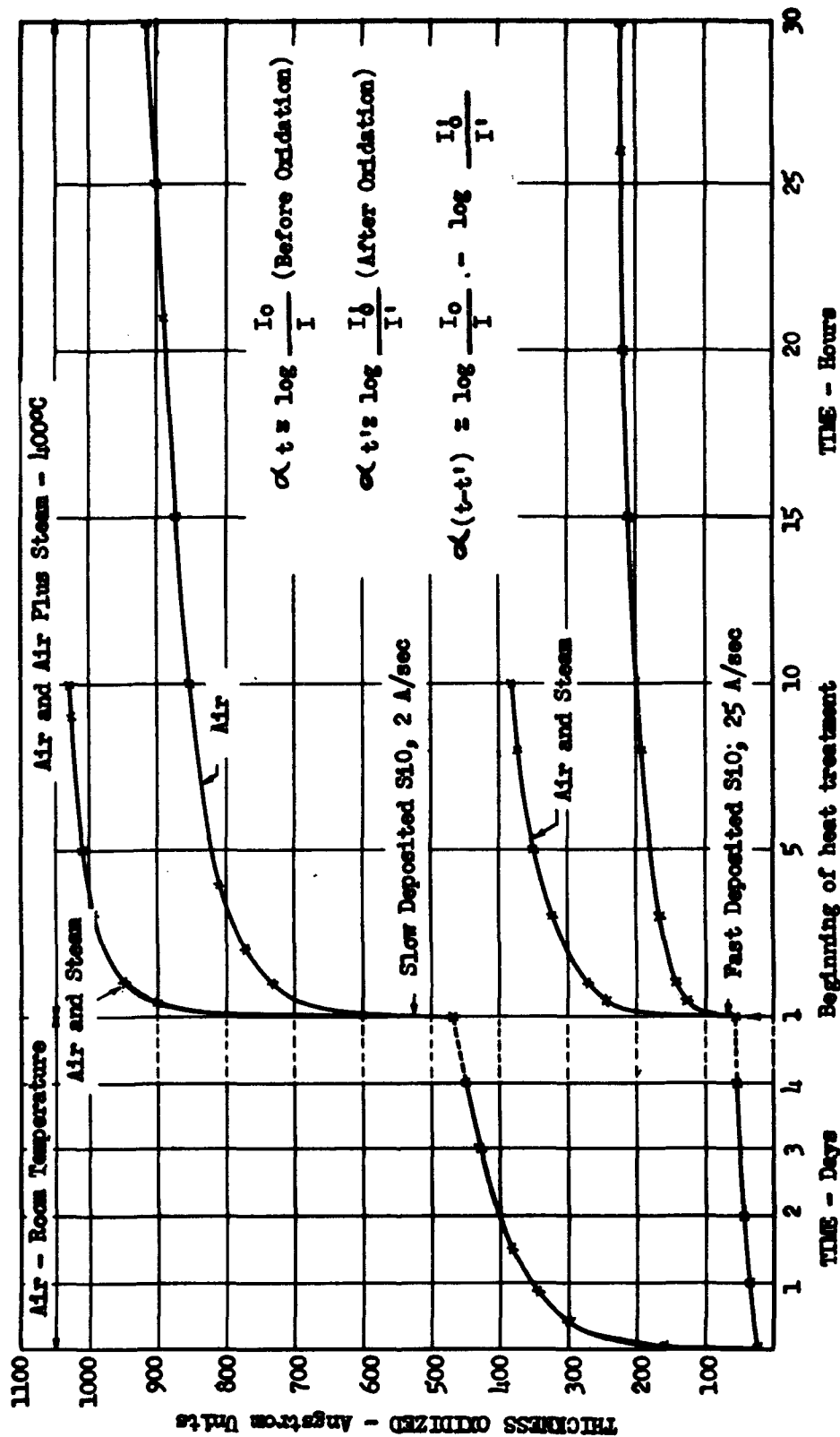
Fig. 8. Comparison of the oxidation rates of fast and slow deposited SiO films calculated from increase in ultraviolet transmission and absorption coefficient α.

$\alpha t = \log \dfrac{I_0}{I}$ (Before Oxidation)

$\alpha t' = \log \dfrac{I_0'}{I'}$ (After Oxidation)

$\alpha(t-t') = \log \dfrac{I_0}{I} - \log \dfrac{I_0'}{I'}$

Air - Room Temperature

Air and Air Plus Steam - 400C

Air and Steam

Air

Slow Deposited SiO, 2 A/sec

Air and Steam

Fast Deposited SiO; 25 A/sec

Beginning of heat treatment

TIME - Hours

TIME - Days

THICKNESS OXIDIZED - Angstrom Units

1100 1000 900 800 700 600 500 400 300 200 100

changes only 170 A of a fast condensed film to silica. The much
looser structure of slow deposited films must be the main reason
for their higher oxidation rates. Both films oxidize much faster
if they are heat treated in air and steam. At 400 C, one hour in
air and steam results in the same oxidizing effect as 30 hours in
normal air. Fig. 9 demonstrates the influence of the evaporation
conditions on the oxidation rates of vacuum-deposited silicon
monoxide films in air at room temperature over 54 days. The faster
the films are deposited, and the better the vacuum is during their
condensation, the lower are their oxidation rates.

IV.   DECOMPOSITION OF SILICON MONOXIDE AT HIGH TEMPERATURES
AND ITS EFFECT ON THE OPTICAL PROPERTIES OF SILICON MONOXIDE FILMS

If a vacuum-deposited thin film of silicon monoxide is heated
in an inert atmosphere instead of air, it remains unchanged up to
temperatures of about 600 C but it decomposes to silicon and silica
when exposed to higher temperatures for several hours. Fig. 10
shows the electron diffraction patterns of a silicon monoxide film
before and after heating in argon at 700 and 900 C. Table II com-
pares the d-values of an untreated and heat-treated silicon monoxide
film with those of vacuum-deposited amorphous and crystalline sili-
con coatings. Silicon is amorphous when it is condensed on bases at
temperatures less than 600 C and forms crystalline films when it is
deposited at higher temperatures.[16] The untreated film shows the
previously mentioned single halo characteristic of true silicon mon-
oxide. After the film has been heated in argon at 700 C for 2 hours
its pattern has completely changed and consists of several diffuse
rings identical with those obtained from a mixture of amorphous
silicon and silica. After heating at 900 C, silicon is crystallized
and the pattern of the film shows only relatively sharp diffraction
rings of silicon and halos of silica. In other words, film material
is completely decomposed to silicon and silica.

The decomposition of silicon monoxide demonstrated with these
electron diffraction patterns changes the optical properties of such
films remarkably. Fig. 11 shows the transmission and reflection
curves of a thin vacuum-deposited silicon monoxide film before and
after one hour of heating in argon at 800 C. The heat-treated de-
composed film has a much lower and higher absorption in the visible
and ultraviolet than has the untreated silicon monoxide coating.
Measurements of transmission of and reflection, can, therefore, be
used to study the beginning of decomposition and to distinguish
between the oxidation and decomposition of silicon monoxide. Oxi-
dation increases while decomposition decreases the ultraviolet
transmission of silicon monoxide films.

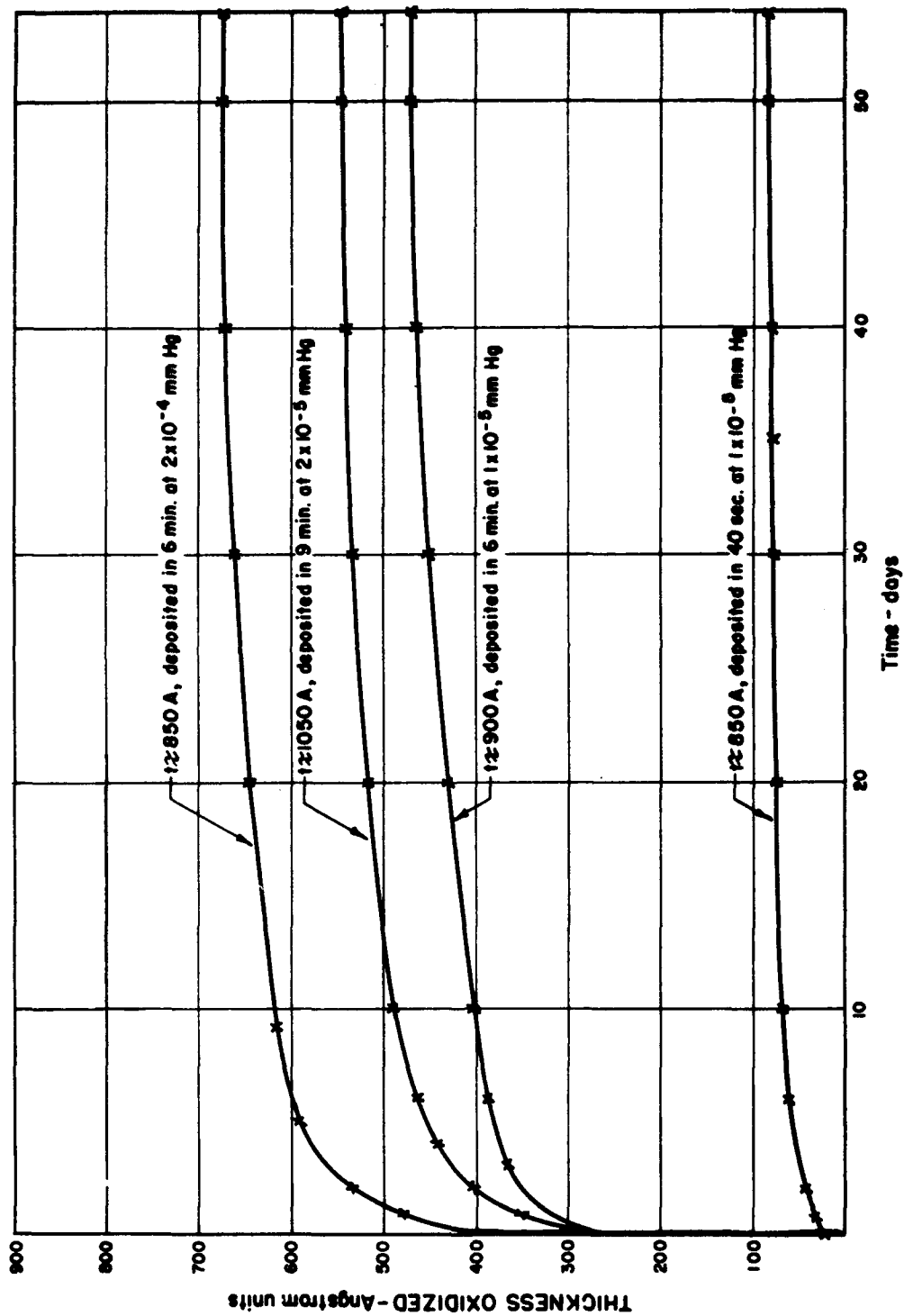16.   G. Hass, Zs. f. anorg. Chem. 257, 166 (1948).

Fig. 9. Oxidation of SiO films produced under various evaporation conditions in air at room temperature. (SiO evaporated from tantalum boat at 18 inches distance.)
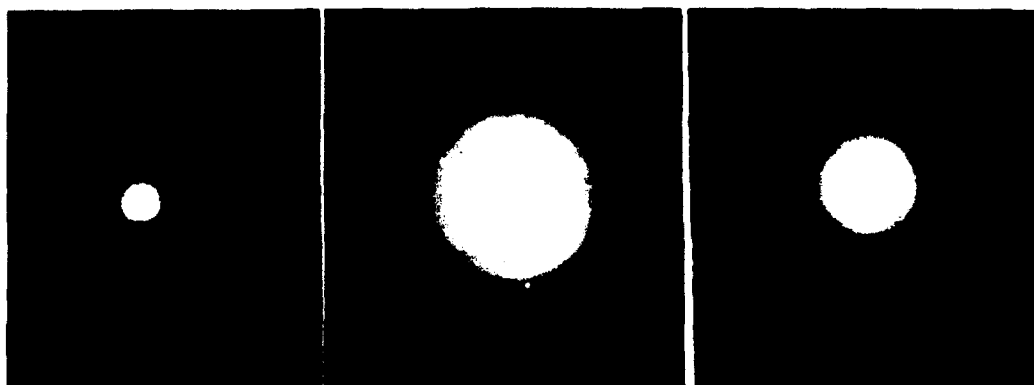
15

461

Fig. 10. SiO film about 600 A thick; (left) untreated;
(center) after 2 hours heating at 700 C in argon; (right)
after 2 hours heating at 900 C in argon.

Table II. Bragg Spacings of a SiO-film before and
after Heating in Argon, Compared with Those of
Amorphous and Crystalline Silicon

Bragg Spacings (d-values in Angstroms)				
SiO before and after Heating in Argon			Amorphous and Crystalline Silicon	
Untreated	2 hr at 700 C	2 hr at 900 C	Si Condensed at 20 C Diffuse Rings	Si Condensed at 680 C Sharp Rings
		4.10 (diffuse)		
3.60 (diffuse)	3.70 (diffuse, very broad)	3.15 (sharp)	3.13	3.15 (very strong)
		1.92 (sharp)		1.92 (strong)
	1.75 (diffuse)		1.75	
		1.635 (sharp)		1.635 (strong)
				1.565 (very weak)
				1.355 (very weak)
		1.245 (sharp)		1.245 (medium)
	1.20 (diffuse)	1.20 (diffuse)	1.20	
		1.105 (sharp)		1.105 (medium)

To study the decomposition of silicon monoxide at elevated
temperatures thin films of this material were also heated in high
vacuum produced by an oil diffusion pump and examined by the
electron diffraction method. After films are exposed to 800 C
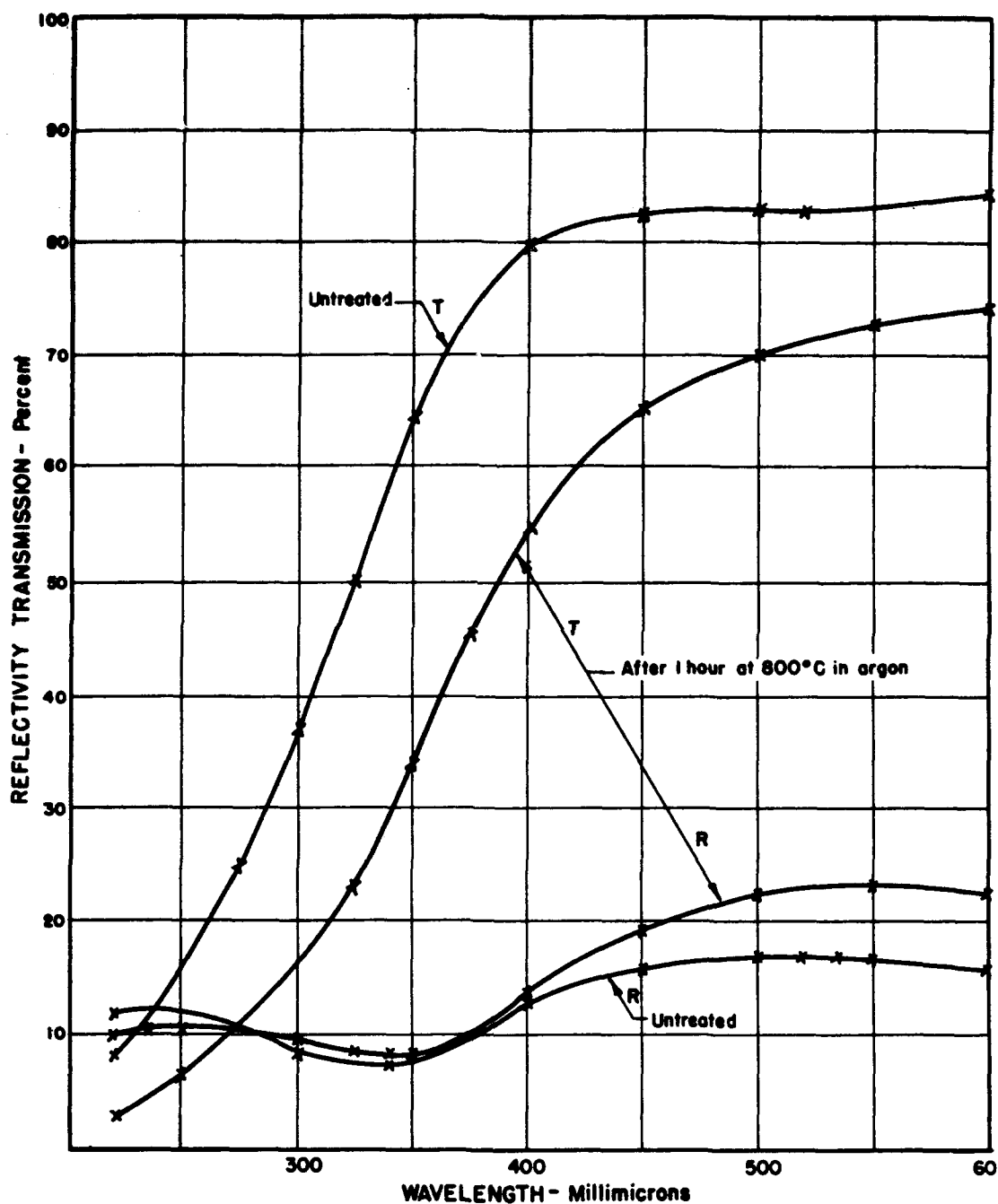for 2 hours their pattern shows rings of silicon and silica .

Fig. 11. Reflectivity and transmission of a SiO film, before and after heating for one hour in argon, as a function of wavelength. (SiO-film about 750 A thick evaporated onto a SiO₂ plate at approximately 2 x 10⁻⁵ mm Hg from a tantalum boat heated to 1170 C.)
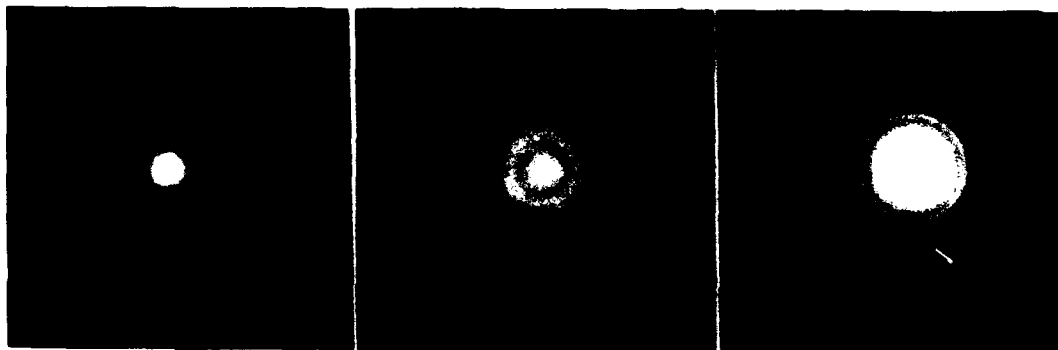
Fig. 12. Electron diffraction patterns of a silicon mon-
oxide film about 600 A thick before and after heating in
vacuum of about 1 x 10⁻⁵ mm Hg produced by an oil diffusion
pump. After heating at 850 C for 2 hours pattern consists
of halos of SiO_2 and rings of β silicon carbide.

If, however, the heat treatment is continued at 850 or 900 C the
silicon rings disappear and become replaced by those of cubic
silicon carbide, in which the lattice constant, a, equals 4.35 A.
Fig. 12 shows the electron diffraction patterns of a silicon
monoxide film before and after heating in a vacuum of about
1 x 10⁻⁵ mm Hg at 800 and 850 C.

On heating to 850 C in a vacuum of an oil diffusion pump the
precipitated silicon of the decomposed silicon monoxide film is
changed to silicon carbide. The cracking of oil molecules on
heated surfaces furnishes the carbon for this reaction.

V. SILICON MONOXIDE FILMS AS REPLICA AND SUPPORTING MEMBRANES FOR ELECTRON MICROSCOPE AND ELECTRON DIFFRACTION INVESTIGATIONS

It has been mentioned previously that silicon monoxide is
especially suitable for preparing replica and supporting mem-
branes for electron microscope and electron diffraction studies.
As is generally known, only very thin specimens can be examined
with the high resolving electron microscope and with the electron
diffraction transmission method. The preparation of extremely
thin completely structureless supporting and replica films is
therefore of basic importance for such examinations. By evapo-
rating silicon monoxide, unsupported films with a thickness down
to 150 A can be produced. These films are amorphous and free of
grain structure and can be subjected to very intense electron
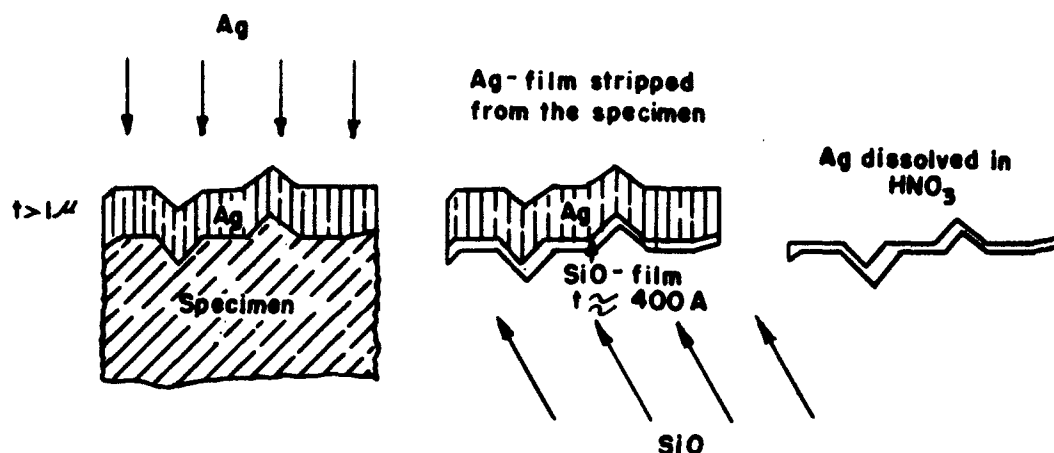bombardment and to heat treatments without breakage and change.

Fig. 13. Method for preparing SiO replica films.

By using a two-step process similar to the silver-collodion one
first suggested by Zworykin and Ramberg,[17] silicon monoxide rep-
licas of most surfaces can be made without damaging the specimen.
The technique is explained in Fig. 13. The specimen to be studied
is placed in a vacuum chamber and a thick layer of silver is
evaporated onto its surface. The silver, which always has poor
adherence, is pulled off the surface with scotch tape and a thin
film of silicon monoxide is evaporated onto the side of the
silver layer which has been in contact with the specimen. To
obtain replicas with good contrast the evaporation of the silicon
monoxide is performed at a 45° angle of incidence. The silicon
monoxide replica is now separated from the silver layer by dis-
solving the silver in nitric acid. Fig. 14 shows silicon mon-
oxide replicas of a 30,000 lines per inch grating prepared by
this method. The grating replicas produced by evaporating sili-
con monoxide at a 90° angle of incidence show sharp dark lines and
are, therefore, especially suitable for calibrating the magni-
fication and for measuring particle sizes exactly. If silicon
monoxide is evaporated at an angle of 45°, the replica shows
more details of the grating surface, as can be seen in Fig. 14.
Silicon monoxide replicas have been made from the original grat-
ing more than 30 times without changing its appearance. Fig. 15
demonstrates the general applicability of the silver-silicon
monoxide replica method. It shows the surface of TlBr-TlI single
crystals (KRS-5) after heat treatments. If a KRS-5 crystal is
heated, it starts to evaporate far below its melting point and
forms pits or etching patterns of regular shape. The shape of
the pits depends on the crystal orientation and is octahedral on

17. V.K. Zworykin and E. G. Ramberg J. App. Phys. 12, 692 (1941).

174-3-35

Fig. 14. Ag-SiO replicas of 30,000 lines per inch grating
Left: SiO evaporated at a 90° angle of incidence. Right:
SiO evaporated at a 45° angle of incidence.

the (100) plane. The etching by heat treatment can be used to
determine the orientation of such crystals.

Fig. 16 demonstrates the use of silicon monoxide films as
supporting membranes for electron diffraction studies. It shows
the diffraction pattern of an aluminum film evaporated onto a
thin "SiO-support." The supporting film is 150 A thick and, if
not deposited extremely fast, completely oxidizes to silica. Its
pattern, which consists only of halos, has practically no in-
fluence on the intensity and sharpness of the aluminum rings.
Such supporting films remain amorphous up to 950 C and are there-
fore especially suitable to study the crystallization, diffusion,
and oxidation of evaporated materials at high temperatures.

174-3-34

Fig. 15. Ag-SiO replicas of TlBr-TlI crystal (100) plane after being heat treated for 20 hours. Top left: 200 C. Top right: 260 C. Bottom left: 275 C. Bottom right: 300 C.
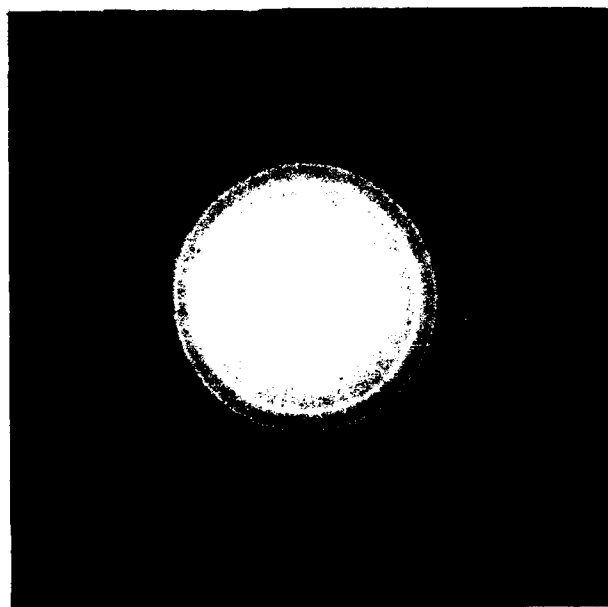

Fig. 16. Electron diffraction pattern of aluminum deposited on a 150 A thick supporting membrane of silicon monoxide.

22

Submitted by:

Georg Hass.

GEORG HASS
Consultant
Radiation Branch

Forwarded by:

Fred W Paul

FRED W. PAUL
Chief, Radiation Branch

Approved 7 September 1950 by:

Oscar P Cleaver

OSCAR P. CLEAVER
Chief, Mechanical and Electrical
          Engineering Department

APPROVAL OF

Report 1180

PROPERTIES, OXIDATION, DECOMPOSITION, AND

APPLICATIONS OF THIN FILMS OF SILICON MONOXIDE

7 September 1950

and

Distribution

465

ADDRESS REPLY TO
COMMANDING OFFICER
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FORT BELVOIR, VA.

IN REPLY
REFER TO:

TECHD ASI
8-23-02-002

2 NOV 1950

SUBJECT: Transmittal of Report 1180, Properties, Oxidation, Decomposition, and Applications of Thin Films of Silicon Monoxide

THRU: Commanding General
The Engineer Center and Fort Belvoir
Fort Belvoir, Virginia

TO: Chief of Engineers
Department of the Army
Washington 25, D. C.
ATTENTION: Chief, Engineer Research and Development Division

1. Transmitted herewith is Report 1180, "Properties, Oxidation, Decomposition, and Applications of Thin Films of Silicon Monoxide," dated 7 September 1950, which was prepared by the Technical Staff of the Engineer Research and Development Laboratories.

2. The report demonstrates that a material satisfying the chemical formula for silicon monoxide can be made by controlled condensation of vapors obtained by heating finely divided silicon and silica in vacuum. Silicon monoxide is structurally different from either silicon or silicon dioxide, and exists only in amorphous form. The relatively low temperature at which silicon monoxide evaporates, its amorphous structure, and the good chemical and mechanical resistance of thin films of this material make it especially suitable for producing protective layers on front-surface mirrors and for preparing replica and support films for electron microscope and electron diffraction studies. Unlike silicon dioxide, silicon monoxide absorbs strongly in the ultraviolet. The increase in ultraviolet transmission of silicon monoxide films in air at various temperatures has been used to measure their oxidation to silicon dioxide. Slow deposited films of silicon monoxide oxidize more rapidly and deeper than fast deposited ones. The looser structure and lower density of slow condensed films accounts for this difference in oxidation behavior. When a vacuum-deposited thin film of silicon monoxide is heated in an inert atmosphere, it remains unchanged up to temperatures of about 600 C, but it
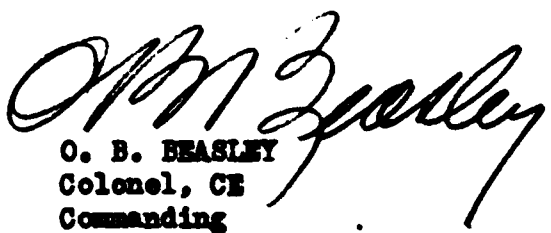
466

TECRD ASI
S-25-02-002
Subject: Transmittal of Report 1180, Properties, Oxidation, Decomposition,
and Applications of Thin Films of Silicon Monoxide

decomposes to silicon and silica when exposed to higher temperatures for
several hours. The heat-treated decomposed film has higher absorption in
the visible and ultraviolet than has the untreated silicon monoxide coating.
On heating to between 850 and 900 C in a vacuum of an oil diffusion pump
the precipitated silicon of the decomposed films of silicon monoxide is
changed to silicon carbide. The cracking of oil molecules on heated sur-
faces furnishes the carbon for this reaction. Methods for preparing replica
and support films of silicon monoxide and their various uses for electron
microscope and electron diffraction studies are described.

3. The report and its contents are approved.

2 Incls   O. B. BEASLEY
  1. Proposed distr list   Colonel, CE
       (in quint)   Commanding
  2. Rpt 1180 (in quad)

TECAG 319.1   1st Ind

    Hq, The Engr Cen & Ft Belvoir, Ft Belvoir, Va.   3 NOV 1950

    TO: C of Engrs, DA, Washington 25, D. C.

2 Incls
  N/C

SUBJECT: Transmittal of Report 1180, Properties, Oxidation, Decomposition, and Applications of Thin Films of Silicon Monoxide

ENGNA (2 Nov 50)   2nd Ind

Office of the Chief of Engineers, Washington 25, D. C., 10 November 1950

TO: Commanding General, The Engineer Center, Fort Belvoir, Virginia

The report, including the proposed distribution list, is approved.

BY ORDER OF THE CHIEF OF ENGINEERS:

2 Incls
w/d

D. G. HAMMOND
Lt. Colonel, Corps of Engineers
Chief, Engr Res & Development Div
Military Operations

TECAG 3/9. 1   2nd Ind

Hq, The Engr Cen & Ft Belvoir, Ft Belvoir, Va.   14 NOV 1950

TO: CO, E.R.D.L., Ft Belvoir, Va.

46

DISTRIBUTION

Corps of Engineers

Chief, Engineer Research & Development Div (4)
Chief, Engr Organization & Training Div (1)
Ch, New York District Office (1)
Engineer School Library (1)

Army Field Forces

Chief, AFF, Engr Sec (1)
President, AFF Board No. 1 (2)
President, AFF Board No. 2, Engr Sec (2)
President, AFF Board No. 3 (1)
President, AFF Board No. 4 (1)

U. S. Air Force

HQ, USAF, DCS/D, R&D Directorate (1)
CS, DC/S Materiel, Dir of Installations (1)
CS, DC/S Materiel, Dir of Research & Development (1)
CS, DC/S Operations, Dir of Requirements (1)
CG, Air Proving Ground (2)
CG, Strategic Air Command (1)
CG, Continental Air Command (2)
CG, Air Training Command (1)
CG, AMC, Equipment Lab (1)
CG, AMC, Materials Lab (1)
CG, Air University (2)
Cmdr, Military Air Transport Serv (1)

Navy

Office of Naval Communication (1)
Bureau of Aeronautics (4)
Bureau of Ordnance (2)
Bureau of Ships, Code 947 (1)
Naval Research Laboratory (2)
Office of Naval Research (1)
Office of Naval Research, Physics Sec (1)
Naval Ordnance Test Station, Photographic Sec (1)
Coast Guard Hq, Testing & Development Div (1)
Naval Civil Engr Labs (1)

Ordnance

Chief of Ordnance, Ammunition Develop Div (2)
Chief of Ordnance, Artillery Develop Div (1)

468

Special

      Chief Signal Officer, U. S. Army (2)
      Fire Control Design Div, Frankfort Arsenal (1)
      Joint Communications Committee (4)
      AF Staff College, Librarian (1)
      U. S. Military Academy, Engr Detachment (1)
      Ch, Army Chemical Division (1)
      Central Air Documents Office (5)