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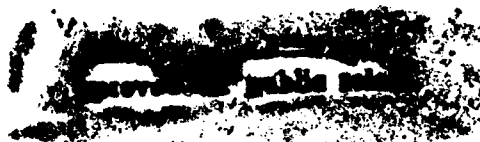
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Report 1180

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

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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 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 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 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 diffraction studies are described.

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 Potter¹ 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 silicon 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) $\text{SiO}_2 + \text{Si} \rightarrow 2 \text{SiO}$
- (2) $\text{SiO}_2 + \text{H}_2 \rightarrow \text{SiO} + \text{H}_2\text{O}$
- (3) $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$
- (4) $\text{Si} + \text{MeO} \rightarrow \text{Me} + \text{SiO}$
- (5) $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{Si} \rightarrow \text{Al}_2\text{O}_3 + 4\text{SiO}$

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

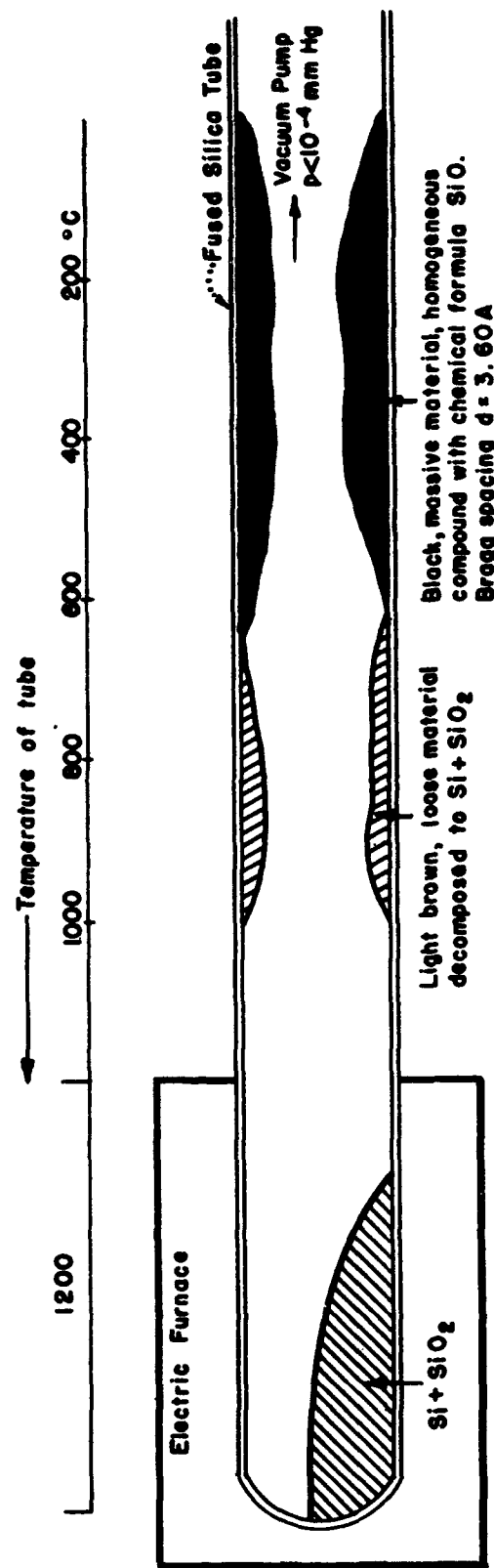


Fig. 1. Arrangement for producing SiO₂.

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 hydrofluoric 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.

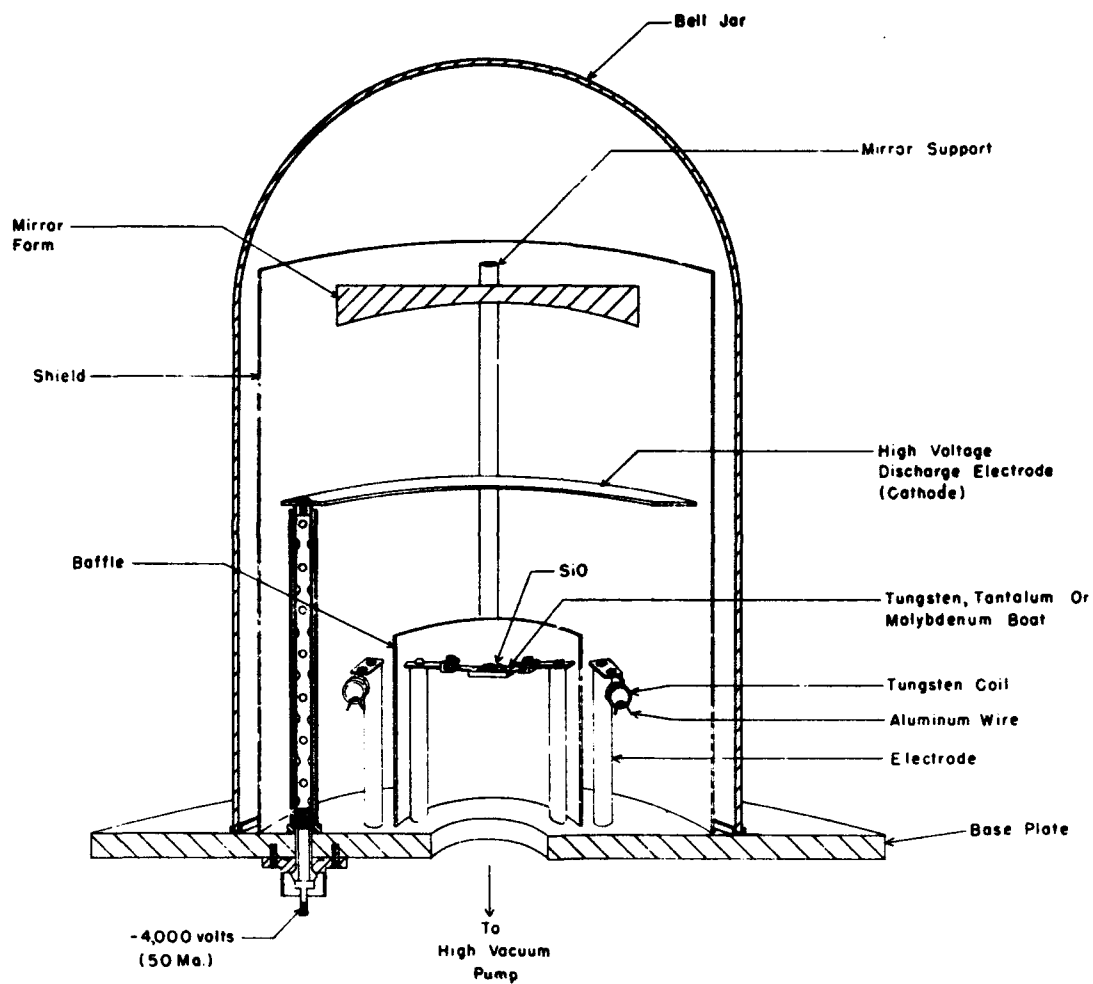


Fig. 2. Vacuum apparatus for preparing silicon monoxide films.

Fig. 3 shows the deposition rates in Angstrom units per second (Å/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 2×10^{-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 Å 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 ($\rho = 2.15$ g per cu cm) and silica glass ($\rho = 2.2$ g per cu cm) but lower than that of silicon ($\rho = 2.40$ 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 $d = 3.65 \pm 0.05$ Å 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).

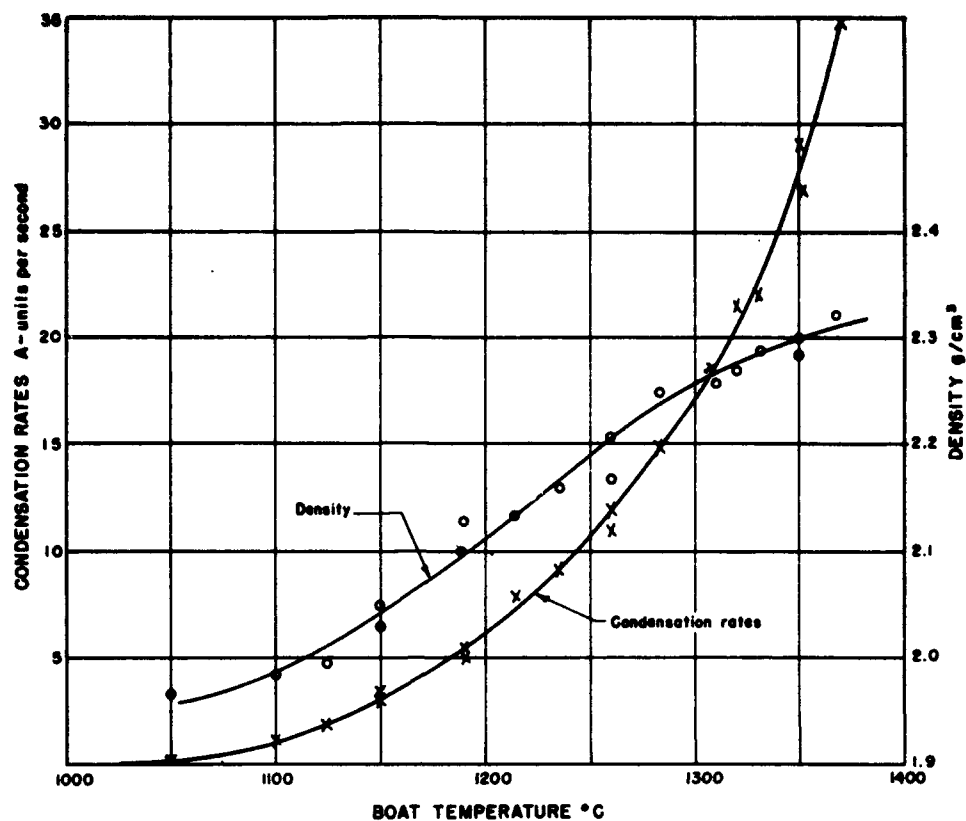


Fig. 3. Rate of condensation and density of film deposited as functions of boat temperature.

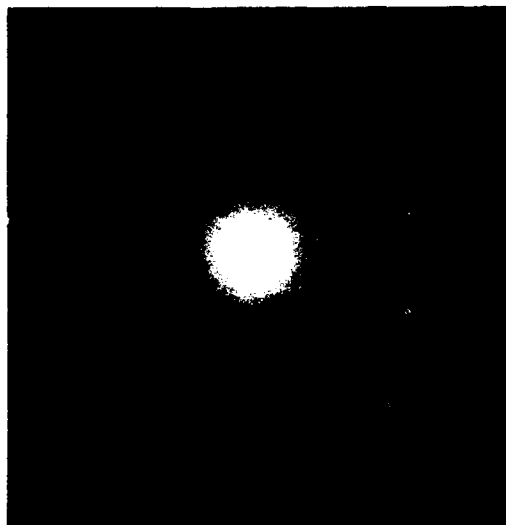


Fig. 4. Electron diffraction pattern of a vacuum-deposited SiO film.

of about 1350 C the halo of the condensed film corresponds to $d = 3.45 \pm 0.05$ 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 solution 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 dioxide by heating them in air. Slow deposited films oxidize much faster and at lower temperatures than the more compact, fast condensed 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 α -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 Warren¹⁴ and Koenig¹⁵ are listed in Table I. The agreement is rather good.

Table I. Bragg Spacings and Estimated Intensities of the Halos

Ring No.	Bragg Spacing (d -values in Angstroms)		
	Electron Diffraction Pattern		X-ray Diffraction
	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).

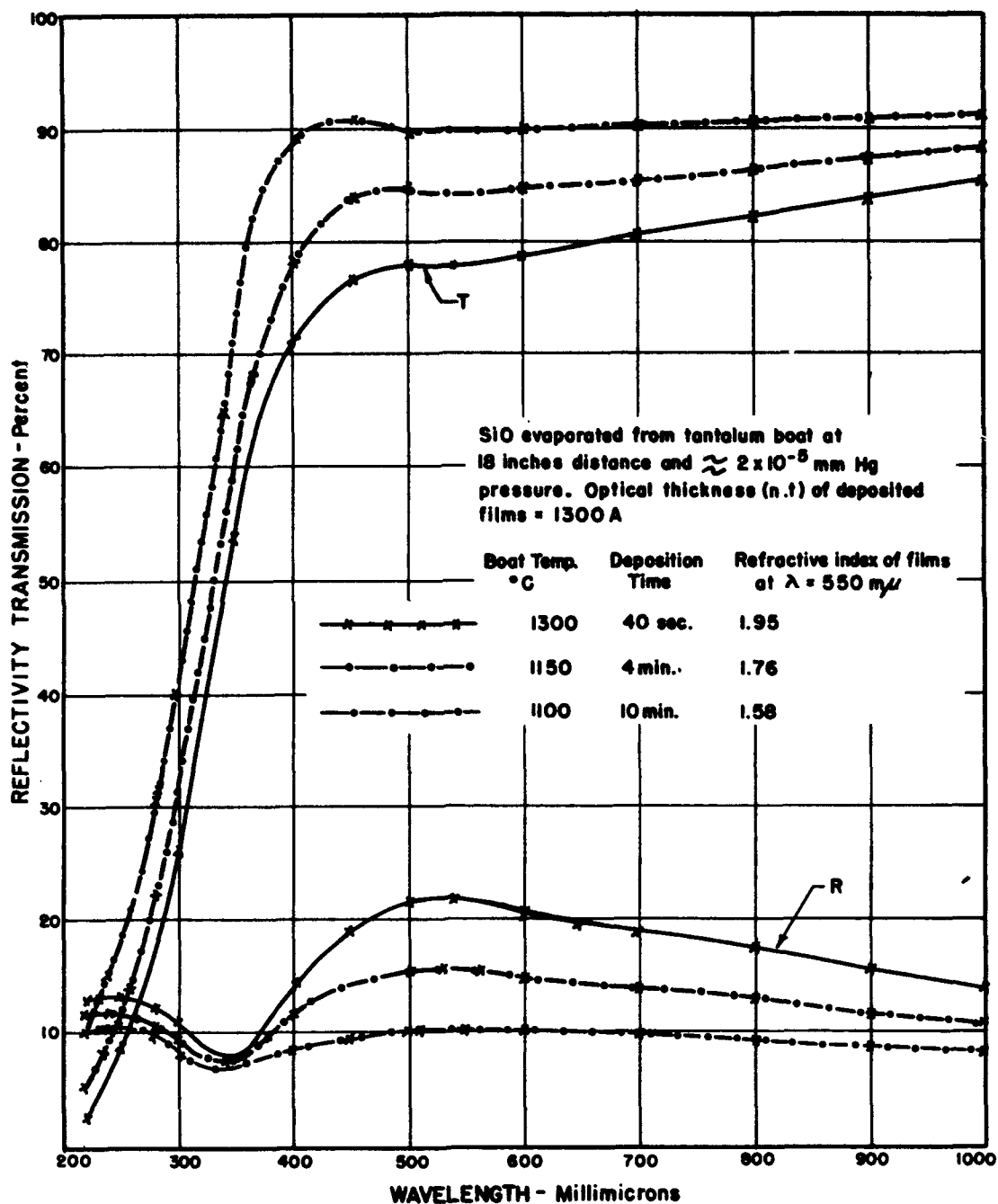


Fig. 5. Reflectivity and transmission of SiO films evaporated on SiO₂ plates at various speeds, as function of wavelength.

Thin films of silicon monoxide were evaporated onto ultraviolet transparent silica plates and their ultraviolet absorption was measured before and after exposure to air at various temperatures. The decrease 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 Å. Their absorption in the visible and infrared region is very small but it is high in the ultraviolet. The ultraviolet absorption and the refractive 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 becomes 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 difference in oxidation behavior is even more evident at higher temperatures. 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 transmission by means of the third equation shown in Fig. 8. The absorption coefficient of the unoxidized material, α , can be determined by the first equation if the film thickness is measured. $(t - t')$ is the thickness of silicon monoxide which is oxidized to silica. $\frac{I_0}{I}$ is the entering intensity divided by the transmitted intensity before oxidation took place, and $\frac{I_0}{I'}$ the same after part of the film is oxidized. After 5 days in air at room temperature, 460 Å of the slow deposited and only 50 Å 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 Å thickness can be completely oxidized at 400 C in a few hours while the same treatment

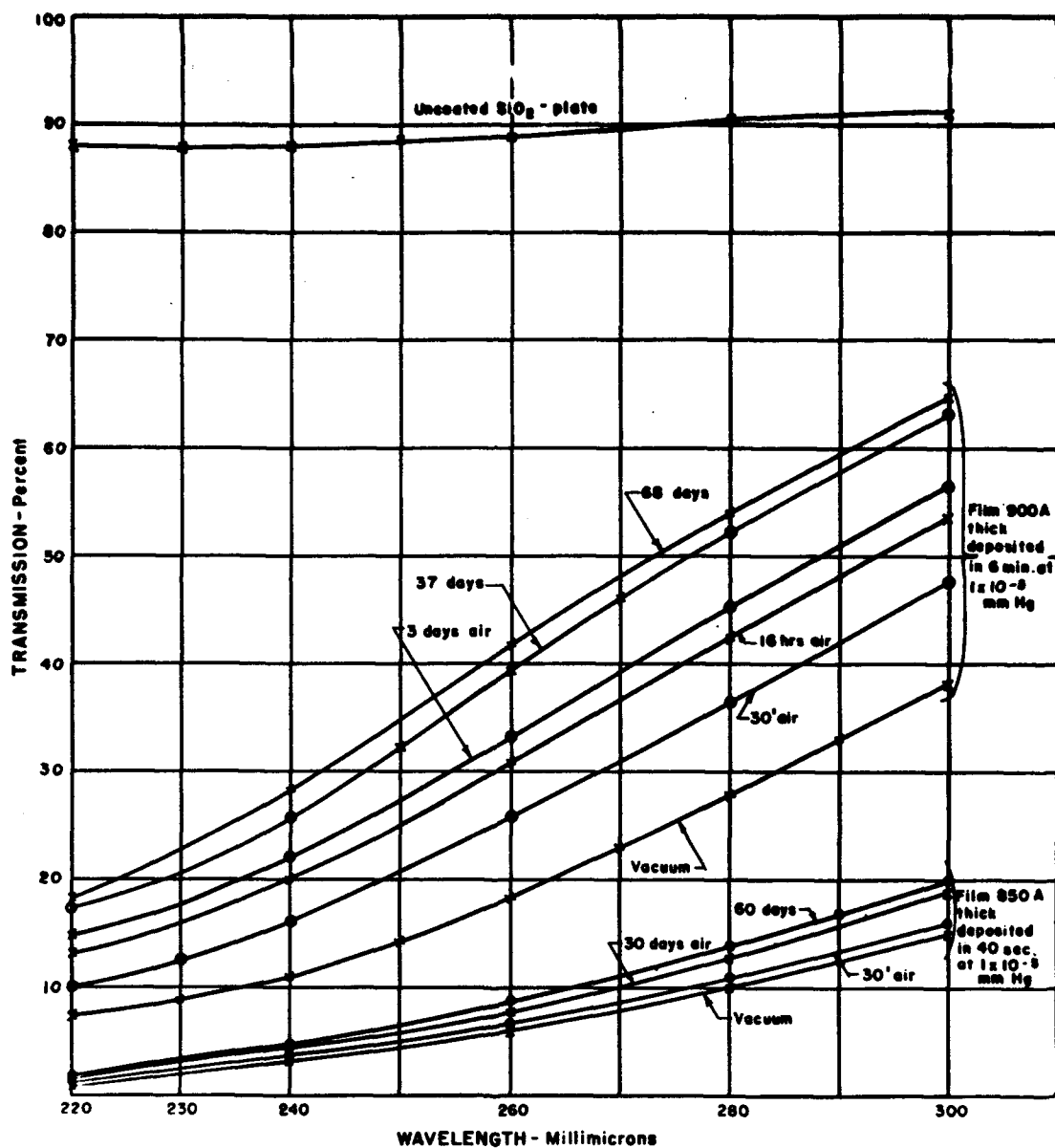


Fig. 6. Increase of UV transmission of fast and slow deposited SiO₂ films caused by oxidation in air at room temperature.

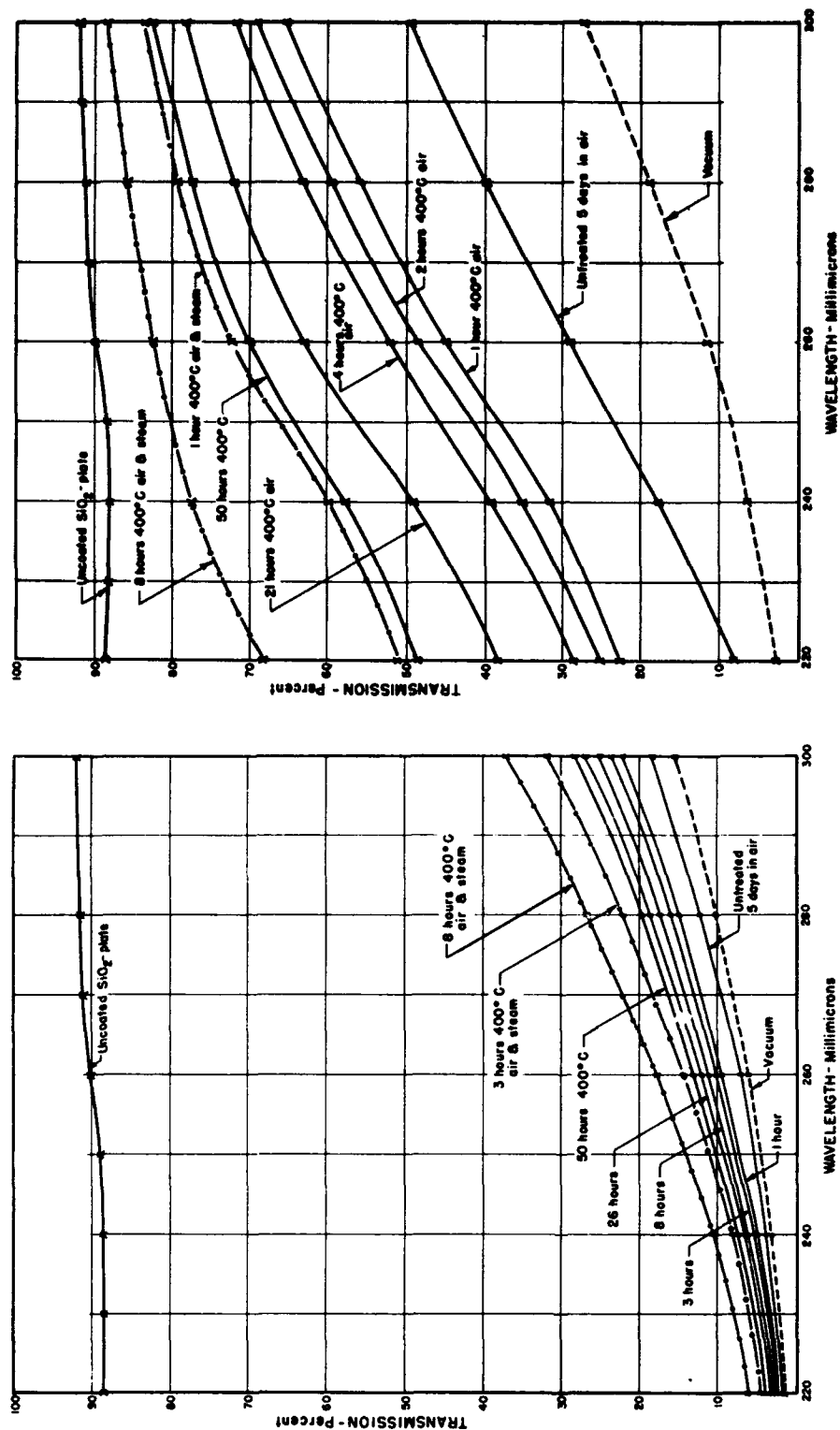


Fig. 7. Change of UV transmission of SiO films caused by oxidation at 400°C in air and in air and steam. Left: Fast deposited SiO film 850 Å thick, deposited in 40 sec at 1×10^{-5} mm Hg. Right: Slow deposited film 1050 Å thick, deposited in 9 min at 2×10^{-5} mm Hg.

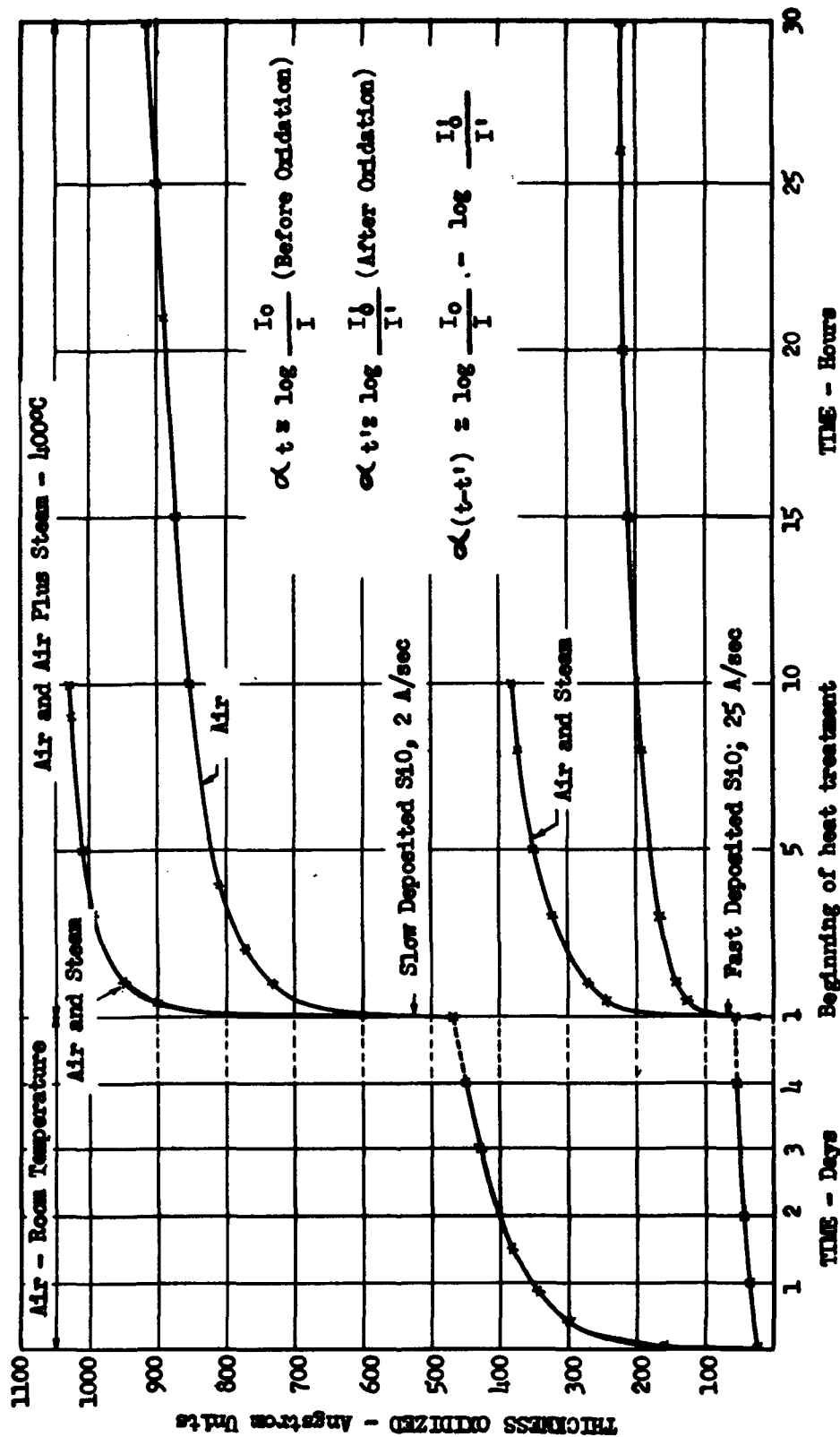


Fig. 8. Comparison of the oxidation rates of fast and slow deposited SiO films calculated from increase in ultraviolet transmission and absorption coefficient α .

changes only 170 Å 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 compares the d-values of an untreated and heat-treated silicon monoxide film with those of vacuum-deposited amorphous and crystalline silicon 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 monoxide. 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 decomposed film has a much lower and higher absorption in the visible and ultraviolet than has the untreated silicon monoxide coating. Measurements of transmission and reflection, can, therefore, be used to study the beginning of decomposition and to distinguish between the oxidation and decomposition of silicon monoxide. Oxidation increases while decomposition decreases the ultraviolet transmission of silicon monoxide films.

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

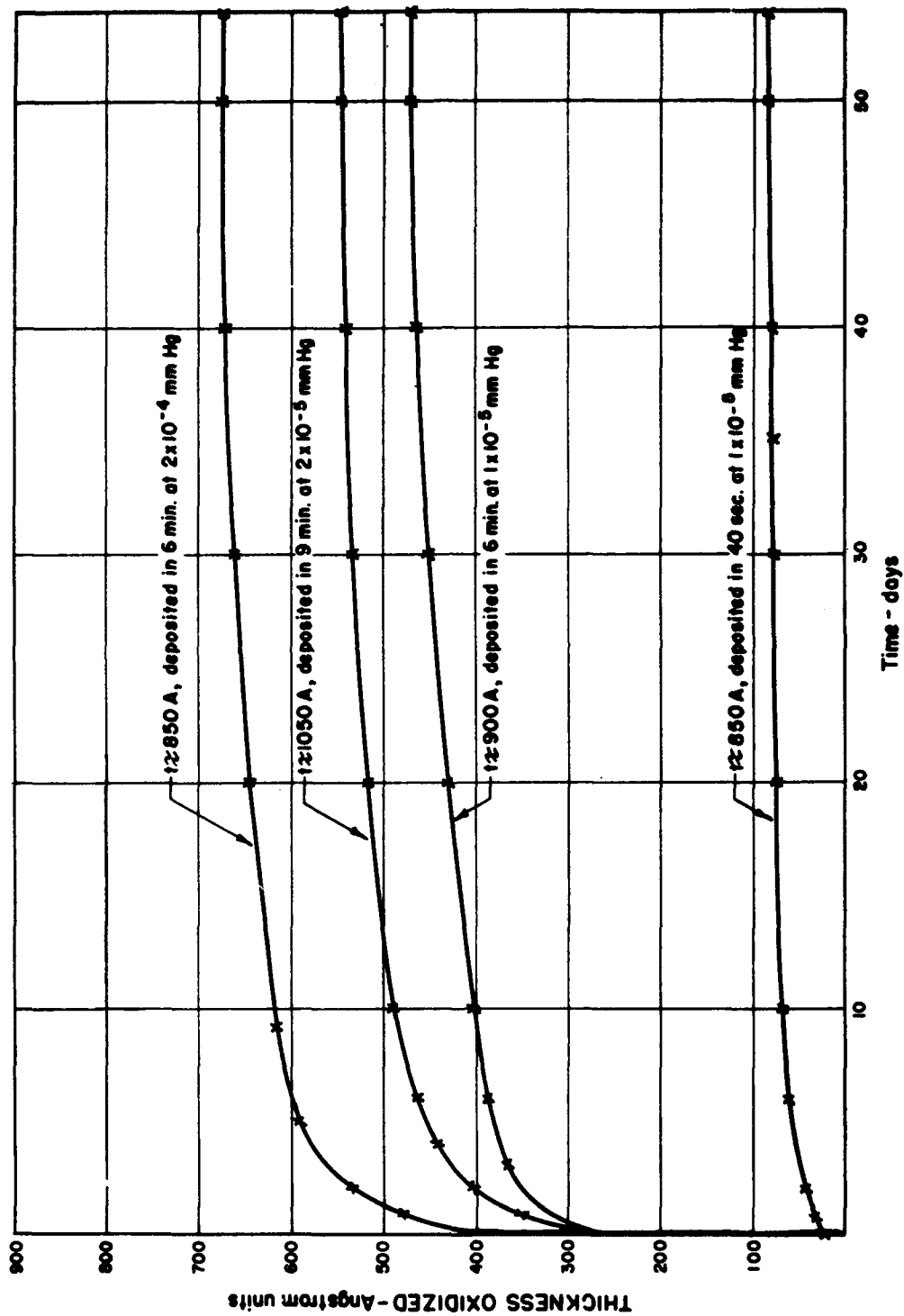


Fig. 9. Oxidation of SiO films produced under various evaporation conditions in air at room temperature. (SiO evaporated from tantalum boat at 18 inches distance.)

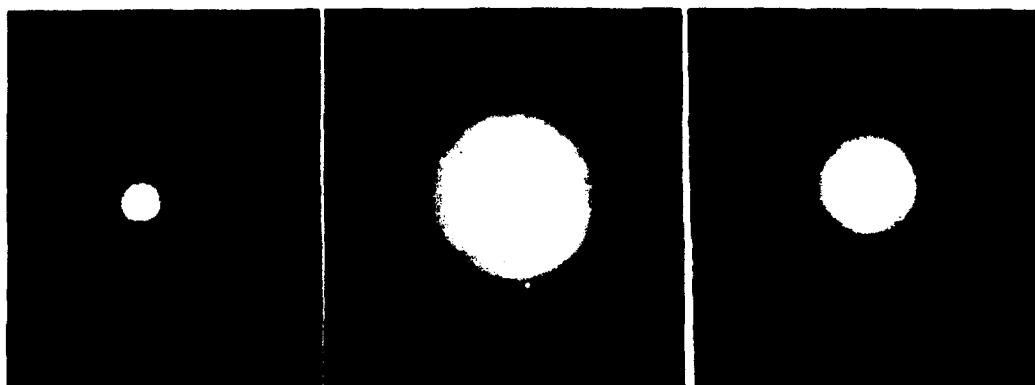


Fig. 10. SiO film about 600 Å thick; (left) untreated; (center) after 2 hours heating at 700 C in argon; (right) after 2 hours heating at 900 C in argon.

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)			Amorphous and Crystalline	
SiO before and after Heating			Silicon	
	in Argon			
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)	1.635 (sharp)	1.75	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.

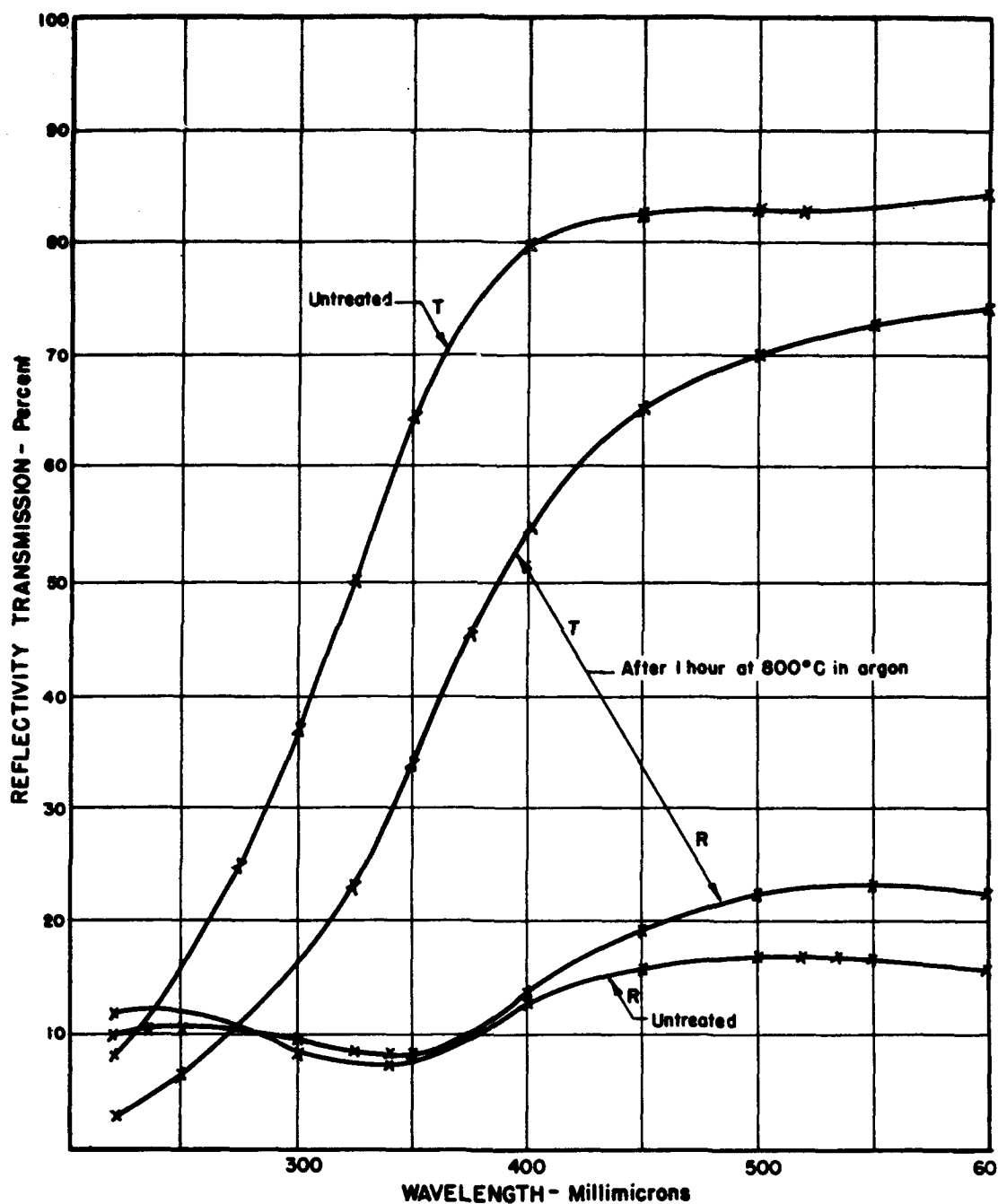


Fig. 11. Reflectivity and transmission of a SiO film, before and after heating for one hour in argon, as a function of wavelength. (SiO-film about 750 Å thick evaporated onto a SiO₂ plate at approximately 2×10^{-5} mm Hg from a tantalum boat heated to 1170 C.)

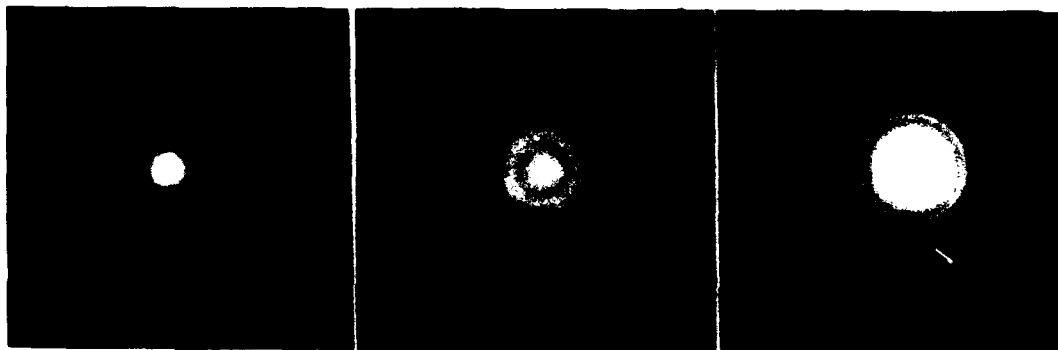


Fig. 12. Electron diffraction patterns of a silicon monoxide film about 600 Å thick before and after heating in vacuum of about 1×10^{-5} mm Hg produced by an oil diffusion pump. After heating at 850 C for 2 hours pattern consists of halos of SiO_2 and rings of β silicon carbide.

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 Å. Fig. 12 shows the electron diffraction patterns of a silicon monoxide film before and after heating in a vacuum of about 1×10^{-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 membranes 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 evaporating silicon monoxide, unsupported films with a thickness down to 150 Å 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.

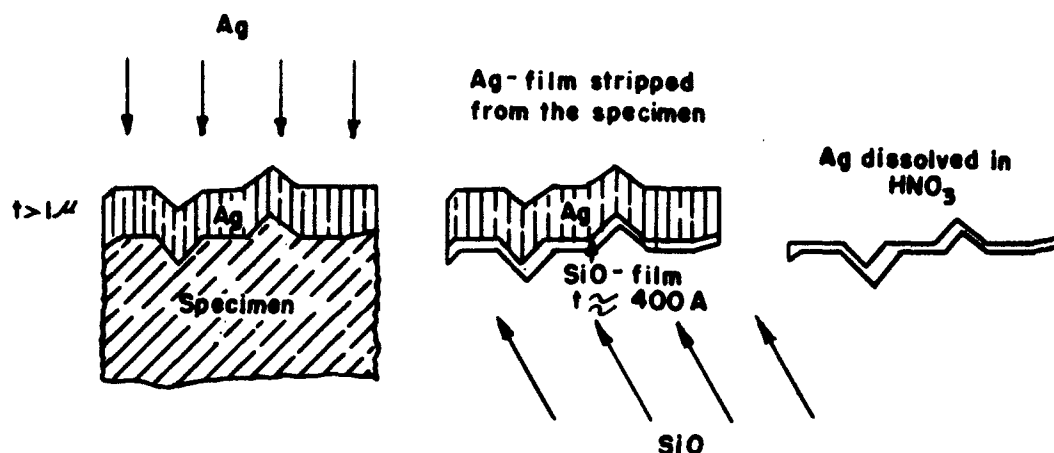


Fig. 13. Method for preparing SiO replica films.

By using a two-step process similar to the silver-collodion one first suggested by Zworykin and Ramberg,¹⁷ silicon monoxide replicas 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 dissolving the silver in nitric acid. Fig. 14 shows silicon monoxide replicas of a 30,000 lines per inch grating prepared by this method. The grating replicas produced by evaporating silicon monoxide at a 90° angle of incidence show sharp dark lines and are, therefore, especially suitable for calibrating the magnification 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 grating 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).

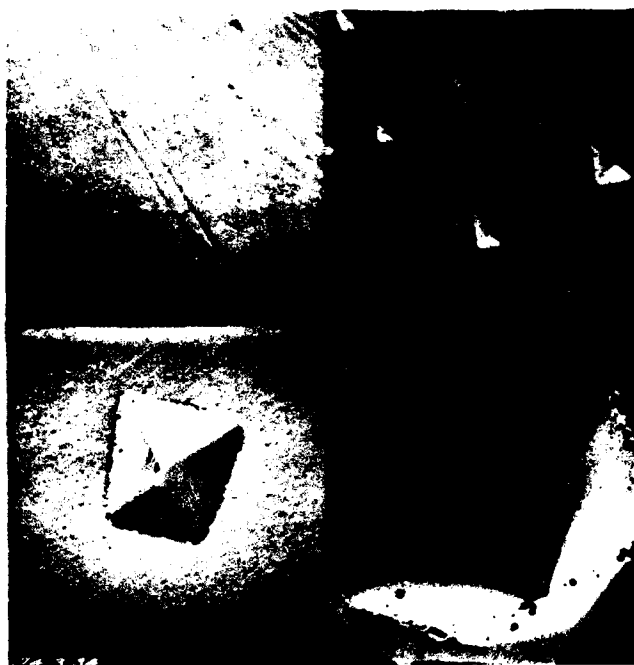


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Fig. 14. Ag-SiO replicas of 30,000 lines per inch grating
 Left: SiO evaporated at a 90° angle of incidence. Right:
 SiO evaporated at a 45° angle of incidence.

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 Å thick and, if not deposited extremely fast, completely oxidizes to silica. Its pattern, which consists only of halos, has practically no influence on the intensity and sharpness of the aluminum rings. Such supporting films remain amorphous up to 950 C and are therefore 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.

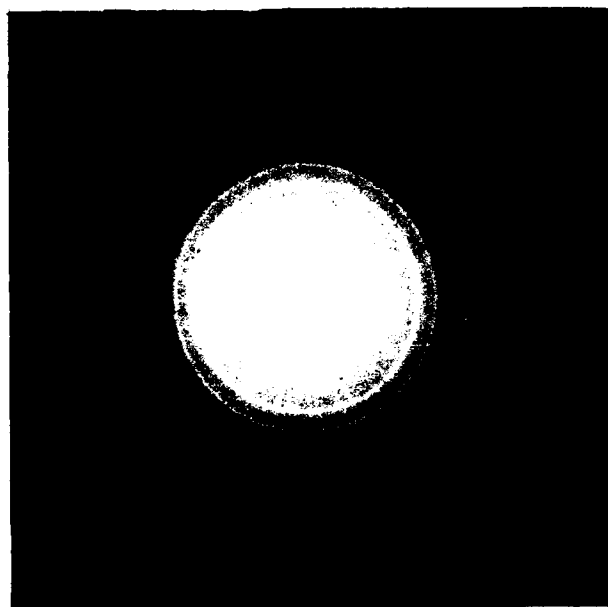


Fig. 16. Electron diffraction pattern of aluminum deposited on a 150 A thick supporting membrane of silicon monoxide.

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

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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

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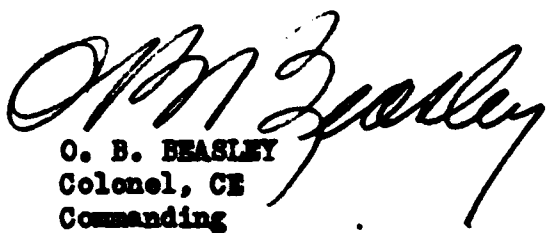
Subject: Transmittal of Report 1180, Properties, Oxidation, Decomposition,
and Applications of Thin Films of Silicon Monoxide

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 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 diffraction studies are described.

3. The report and its contents are approved.

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O. B. BEASLEY
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Commanding

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

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

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