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Optical Properties of Silicon Monoxide in the Wavelength Region from 0.24 to 14.0 Microns*

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Using evaporation conditions adjusted for the deposition of true silicon monoxide, a series of films ranging in thickness from 0.03 to 10 microns was prepared on fused quartz, glass, rock salt, and highly reflecting aluminum surfaces. The optical constants of the films were computed in the wavelength region from 0.24 to 14 microns from reflectance, transmittance, and thickness measurements. Silicon monoxide films exhibit strong absorption in the ultraviolet which extends into the visible, and an infrared absorption maximum at 10 microns which differs significantly from the position of the absorption maximum of fused quartz. In the wavelength region from 0.40 to 0.70 micron, the refractive index of SiO decreases with increasing wavelength from 2.15 to 1.95. Strongly oxidized films show less ultraviolet absorption, lower indexes of refraction, and a shift of the infrared absorption band to shorter wavelength. Decomposition of SiO to $Si+SiO_2$ results in increased ultraviolet absorption and higher refractive indexes. In the region of the 10-micron absorption a silicon monoxide protective layer of 0.125 micron in thickness has no appreciable effect on the reflectance of a highly reflecting metallic surface, but decreases the transmittance of a rock salt plate by 30 percent.

I. INTRODUCTION

IN recent years, films produced by high vacuum evaporation of silicon monoxide have found many different applications.[1] They have proved to be especially suitable as protective layers on front surface mirrors, and as replica and supporting membranes for electron-microscope and electron-diffraction studies. They are also used extensively in multilayer combinations for increasing and decreasing the reflectance of dielectrics and metals in various spectral regions.[2]

In spite of the frequent use of silicon monoxide as an optical film material, very little quantitative information is available regarding its optical properties, particularly in the ultraviolet and the infrared. This is primarily due to the fact that the optical properties of vacuum-deposited silicon monoxide films can vary appreciably depending on the evaporation conditions imposed during film preparation. It has been established that the gas evolving from a mixture of $Si+SiO_2$, or from prepared silicon monoxide, at evaporation temperatures used for the deposition of films (1150°C to 1250°C), has the composition SiO.[3,4] Most of the condensed films, however, show a composition with more or less excess of oxygen and, therefore, optical properties which are more or less different from those of true SiO. The excess of oxygen is the result of both oxidation during the film condensation process and subsequent exposure to air. As reported,[1] true SiO films can only be prepared by fast deposition (deposition rate ≥ 10A/sec) under good vacuum conditions ($p \lesssim 1\times10^{-5}$ mm Hg). The foregoing conditions minimize the opportunity for oxidation while the material is being condensed and furthermore produce dense films which oxidize very little when exposed to air. (After 2 hours exposure to air only about 20A of the fast-deposited SiO is converted to SiO_2.) If the silicon monoxide is deposited slowly (deposition rate $\lesssim 3$A/sec) in a poor vacuum ($p \sim 1\times10^{-4}$ mm Hg of air) a strongly oxidized incompact film results which has a high rate of oxidation when exposed to air.

* Presented at the meeting of the Optical Society of America, New York, New York, March 19–21, 1953.

[1] G. Hass, J. Am. Ceram. Soc. **33**, 353 (1950). This paper contains an extensive bibliography on the preparation, structure, and application of silicon monoxide films.

[2] Hass, Schroeder, and Turner, J. Opt. Soc. Am. **43**, 326 (1953).

[3] K. F. Bonhoeffer, Z. physik. Chem. **131**, 363 (1928).

[4] H. Schäfer and R. Hörnle, Z. anorg. u. allgem. Chem. **263**, 261 (1950).

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It is the purpose of the present paper to present data on the optical constants of true silicon monoxide films in the wavelength region from 0.24 to 14.0 microns and to furnish additional spectroscopic evidence that the material studied is a true compound and not a mixture of Si and SiO_2. The paper also discusses the effect of oxidation and decomposition on the optical properties of silicon monoxide and gives information on the infrared reflectance and transmittance of silicon monoxide-protected aluminum and rock salt.

II. METHODS USED FOR DETERMINING THE OPTICAL CONSTANTS

The problem consisted of determining the optical constants of a thin film on a nonabsorbing backing plate from experimentally measured values of reflectance, transmittance, and film thickness. The methods used for determining the optical constants differed depending on whether or not the film exhibited appreciable absorption. The more difficult method used in the highly absorbing regions will be discussed first.

The measured reflectance and transmittance of a filmed plate include the effects associated with the unfilmed or second surface of the backing plate. After correcting for this back surface reflection by a method of intensity addition the problem reduces to the case of a thin absorbing film on a semi-infinite nonabsorbing backing. If normal incidence radiation is used for the measurements, the reflectance and transmittance for this case are given by the following equations:[5]

$$R_0=\frac{\left[(n_b-1)\cos\frac{2\pi t}{\lambda}(n_f+ik_f)+i\left[\frac{n_b}{n_f+ik_f}-(n_f+ik_f)\right]\sin\frac{2\pi t}{\lambda}(n_f+ik_f)\right]^2}{\left[(n_b+1)\cos\frac{2\pi t}{\lambda}(n_f+ik_f)-i\left[\frac{n_b}{n_f+ik_f}+(n_f+ik_f)\right]\sin\frac{2\pi t}{\lambda}(n_f+ik_f)\right]^2},$$

$$T_0=\frac{4n_b}{\left[(n_b+1)\cos\frac{2\pi t}{\lambda}(n_f+ik_f)-i\left[\frac{n_b}{n_f+ik_f}+(n_f+ik_f)\right]\sin\frac{2\pi t}{\lambda}(n_f+ik_f)\right]^2},$$

where n_b=index of refraction of the backing plate, t=film thickness, λ=wavelength, n_f=index of refraction of the film, and k_f=absorption coefficient of the film.

These equations interrelate R_0 and T_0 with n_f and k_f since the parameters n_b, t, and λ are known or can be separately determined. Theoretically it should be possible to measure R and T, apply the second surface correction to obtain R_0 and T_0, and then solve the set of equations for n_f and k_f. Actually the equations are so complex that explicit forms for n_f and k_f cannot be found, and trial and error numerical solutions have to be used to determine these parameters.

The complexity of the trial and error process can be reduced by utilizing an additional expression relating n_f and k_f. A thick film in a region of high absorption can be treated as though the film were infinitely thick. This is valid since the radiation transmitted through the first film surface is, for all intents and purposes, completely absorbed in the film and does not reach the film-backing interface. The reflectance of an absorbing medium of infinite extent is given by

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2},$$

when the surface is illuminated at normal incidence. This equation can be inverted to give an explicit expression for n in terms of k and the reflectance of an opaque coating:

$$n=\frac{1+R}{1-R}\pm\left[\frac{4R}{(1-R)^2}-k^2\right]^{\frac{1}{2}}.$$

Both values of n given by this expression can have physical significance and the correct value cannot be decided from the reflectance alone. However, it is known from the theory of anomalous dispersion that the lower value of the index of refraction applies for wavelengths shorter than that at which the absorption maximum occurs, and the higher value applies in the wavelength region beyond the absorption maximum.

A first approximation to the value of k_f at some fixed wavelength can be obtained from the slope of a plot of the logarithm of the transmittance *versus* film thickness. This is evident from the equation defining the absorption coefficient,

$$I=I_0e^{-(4\pi kt/\lambda)} \quad \text{or} \quad \log T\sim-\frac{4\pi Mkt}{\lambda}+A.$$

In practice the curves plotted from the above expressions deviate from straight lines because of change of reflectance with film thickness and the existence of coherent multiple reflections in the film. Nevertheless, a good first approximation to the value of k_f can be obtained from the slope of an average straight line drawn through the dispersed points.

[5] Harris, Beasley, and Loeb, J. Opt. Soc. Am. 41, 604 (1951).

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The procedure used for computing n_f and k_f in a region of high absorption may be summed up as follows:

1. The measured values of R and T were corrected for the contributions from the unfilmed surface of the backing plate by a simple method of intensity addition.
2. Semilog plots of transmittance *versus* film thickness were made at different wavelengths, and first approximations to k_f values were obtained from the slopes of straight lines fitted to the data.
3. A value for n_f was computed using the k_f selected in step number 2 and reflectance of an effectively opaque coating.
4. These values of n_f and k_f were inserted in the exact expressions for the reflectance and transmittance and adjusted to provide the best fit with the experimental data.

In those wavelength regions where the absorption is very small, k_f can be assumed to vanish. The equations for the reflectance and transmittance then reduce to

$$R_0=\frac{\left[(n_b-1)\cos\frac{2\pi n_f t}{\lambda}+i\left(\frac{n_b}{n_f}-n_f\right)\sin\frac{2\pi n_f t}{\lambda}\right]^2}{\left[(n_b+1)\cos\frac{2\pi n_f t}{\lambda}-i\left(\frac{n_b}{n_f}+n_f\right)\sin\frac{2\pi n_f t}{\lambda}\right]^2},$$

$$T_0=\frac{4n_b}{\left[(n_b+1)\cos\frac{2\pi n_f t}{\lambda}-i\left(\frac{n_b}{n_f}+n_f\right)\sin\frac{2\pi n_f t}{\lambda}\right]^2}.$$

When $n_f t=(2m+1)\lambda/4$, then

$$n_f=[n_b(1+R_0^{\frac{1}{2}})/(1-R_0^{\frac{1}{2}})]^{\frac{1}{2}} \quad \text{for} \quad n_f^2>n_b$$

and

$$n_f=[n_b(1-R_0^{\frac{1}{2}})/(1+R_0^{\frac{1}{2}})]^{\frac{1}{2}} \quad \text{for} \quad n_f^2<n_b.$$

With this expression n_f can be directly computed from the value of the reflectance at those wavelengths where the optical thickness of the film is an odd multiple of a quarter wavelength.

If the true thickness of the film is known, additional determinations of n_f can be made by utilizing the fact that the reflectance and transmittance are maxima or minima at those wavelengths where the optical path in the film is some multiple of a half or a quarter wavelength.

III. EXPERIMENTAL TECHNIQUES

The thin films were produced in a vacuum system consisting of a glass bell jar 12 inches in diameter and 24 inches high placed on a metal base plate. The pressure in the vacuum chamber could be reduced to 5×10^{-6} mm Hg and maintained at this pressure throughout the evaporation. Evaporation of the silicon monoxide was accomplished by placing small pieces of the material† in a tantalum boat mounted close to the base plate on insulated copper supports through which currents of several hundred amperes could be passed to heat the boat. The amount of heating current and consequent speed of evaporation was controlled by a variable transformer arrangement. In addition to the rock-salt or fused-quartz substrate plate used for reflectance and transmittance measurements, a glass plate and an aluminized mirror were included in each vacuum deposition. These three plates were 2×2 inches square and were supported eighteen inches above the evaporation source. The coated glass plates were subsequently used for the film thickness determinations. The aluminum mirrors, prepared shortly before each SiO evaporation, were included to study the effect of various SiO protective coatings on the reflectance of aluminum. A removable shutter was placed between the substrate plates and the evaporation source to avoid contamination of the plates while the boat and SiO were being outgassed and brought up to evaporation temperature. Final cleaning of the specimen plates before evaporation was performed in the vacuum system by the usual method of a high-voltage glow discharge. During those depositions which included a rock-salt plate, final cleaning was accomplished by heating the plates to a temperature of 150°C with a coiled nichrome wire heating element placed above the plates. This deviation from the usual procedure was necessary because color centers are produced in rock salt by ionic bombardment during the glow discharge.

Film thickness was controlled during the evaporation process by monitoring the changes in reflectance from one of the sample plates as the film material was deposited. A 550-millimicron filter was used in the vacuum system photometer and film thicknesses were controlled in multiples of a quarter-wavelength optical path in the film. True film thickness was measured by a multiple beam interferometer method.[6] The glass plate, included in each SiO evaporation, was partially masked by a thin piece of sheet metal in order to produce a sharp film boundary on the surface of the glass plate. A thin opaque aluminum coating was then evaporated onto the unmasked plate, providing a highly reflecting surface which accurately contoured the boundary between the filmed and unfilmed part of the measuring plate. Interference fringes were produced in a wedge between the measuring plate and a beam splitter cover plate. The amount of shift in the position of the fringes as they crossed the boundary was used to determine film thickness. The cover plate had a highly reflecting, low absorbing multilayer coating of MgF_2 and TiO_2 which produced extremely sharp fringes with high contrast.

† Silicon monoxide was supplied by the Kemet Laboratories, Division of Union Carbide and Carbon, Cleveland, Ohio.

[6] S. Tolansky, *Multiple Beam Interferometry of Surfaces and Films* (Clarendon Press, Oxford, 1948).

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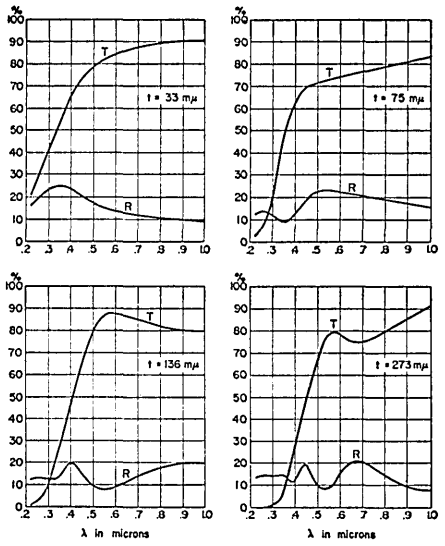

FIG. 1. Transmittance and reflectance of four successively thicker SiO films deposited on fused quartz plates from 0.24 to 1.0 microns.

Reflectance and transmittance measurements between 200 millimicrons and 2.0 microns were made with a Beckman Model DU Spectrometer to which a lead sulfide detector had been added in order to extend the wavelength range to 2.0 microns. Infrared measurements from 2.0 to 14.0 microns were made with a Baird Associates double-beam recording spectrophotometer.

IV. RESULTS

A. Optical Properties of True SiO Films

Figures 1 and 2 show reflectance and transmittance curves of SiO films with various thicknesses, prepared on nonabsorbing backing plates in a vacuum of approximately 1×10^{-5} mm Hg with a deposition rate of 10 to 14A/sec. These curves are representative of all the data obtained and indicate the optical behavior of true SiO in this spectral region. The salient features exhibited by the curves in these two figures are a strong ultraviolet absorption whose edge extends into the visible and an infrared absorbing region which is centered at ten microns.

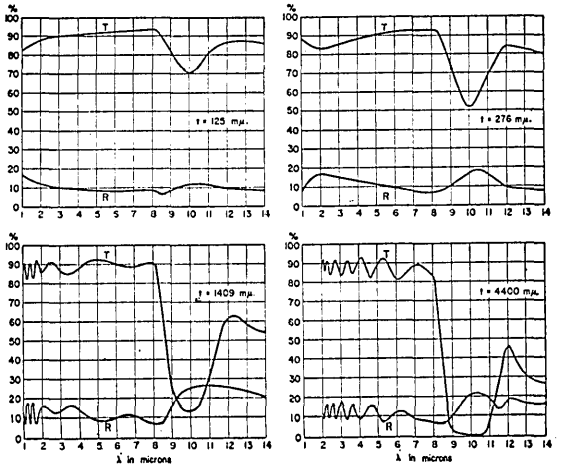

FIG. 2. Infrared transmittance and reflectance of four successively thicker SiO films deposited on rock-salt plates.

The index of refraction and absorption coefficient of SiO were computed by the stepwise procedure previously described. Six sample films with thicknesses between 33 and 400 millimicrons were used in the ultraviolet, and seven sample films with thicknesses varying from 125 to 1950 millimicrons were used in the infrared computations. In the trial and error numerical determinations, adjustment of n and k values was continued until the reflectance and transmittance of the sample films were matched to ±2 percent or better. Typical log-transmittance *versus* film-thickness curves used to estimate the value of the absorption coefficient, and to determine transmittance as function of film thickness in the infrared absorption region are shown in Fig. 3.

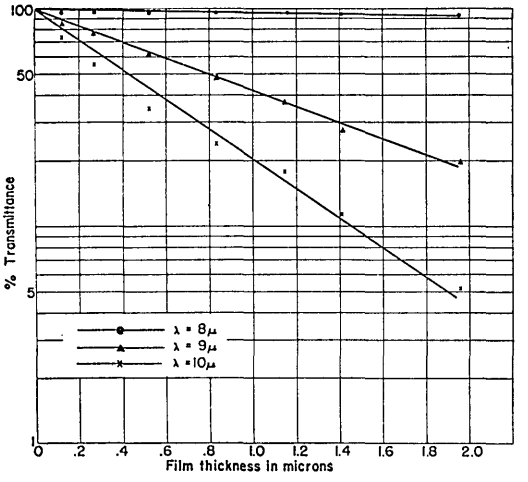

FIG. 3. Semilog plots of transmittance *vs* film thickness used to estimate the absorption coefficient of SiO coatings at different wavelengths.

In the wavelength region where the films exhibit little or no absorption, the refractive indexes were computed for many films of various thicknesses by the three independent methods previously cited. Agreement was found to be within ±1 percent, indicating that the measurements of film thickness, wavelength, reflectance, and transmittance were made to at least this accuracy, and that the refractive indexes of the films studied were independent of film thickness.

The index of refraction and absorption coefficient of silicon monoxide from 240 millimicrons to 14 microns are plotted in Figs. 4 and 5. The over-all accuracy of the curves cannot be simply specified. In the regions of high absorption the constants presented will allow computation of reflectance and transmittance to within ±2 percent; in the wavelength regions where there is

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little or no absorption the reflectance and transmittance can be computed to within ±1 percent.

B. Optical Properties of Oxidized Films

SiO films can be oxidized either by prolonged baking in air after the films have been condensed under good vacuum conditions or by allowing the material to getter oxygen during the deposition process. Oxidation of the films produces significant changes in their optical properties. Figure 6(a) shows the reflectance and transmittance of two fused-quartz plates coated with different deposition rates and at different pressures with films of approximately the same optical thickness. The coating prepared at a much slower deposition rate and at a higher pressure (produced by leaking air into the vacuum chamber during the evaporation) shows a large shift in the absorption edge toward shorter wavelengths, decreased absorption in the ultraviolet and visible regions, and a lower refractive index. Front surface mirrors which are to be used in the visible and

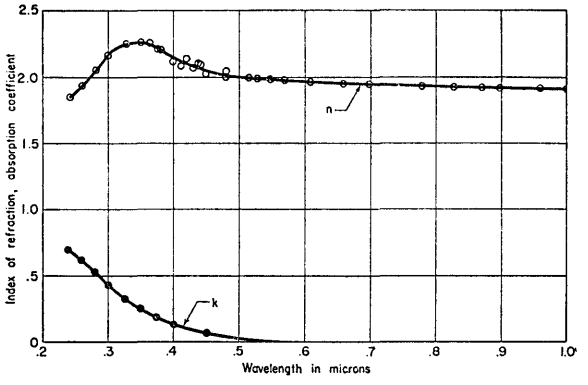

FIG. 4. Index of refraction and absorption coefficient of SiO from 0.24 to 1.0 microns.

near ultraviolet should, therefore, be coated with a partially oxidized film rather than with one of true SiO. In Fig. 6(b) the improved optical performance of an aluminum mirror protected with a partially oxidized film is illustrated by comparing it with the reflectance of a mirror coated with true SiO. The partially oxidized films are less dense than those of true SiO because they are deposited at a much slower rate. However, they make excellent protective coatings since they adhere strongly to most substrates and are hardened rapidly by further surface oxidation when exposed to air.

A dependency exists between the evaporation process parameters (pressure and deposition rate) and the refractive index of the resulting films. It is possible, by controlling pressure and deposition rate, to prepare films with a rather large variation in refractive index. For example, films with good mechanical properties and indexes that vary between 1.55 and 2.00 in the wavelength region between 500 and 700 millimicrons can be produced. This ability to control the refractive index is

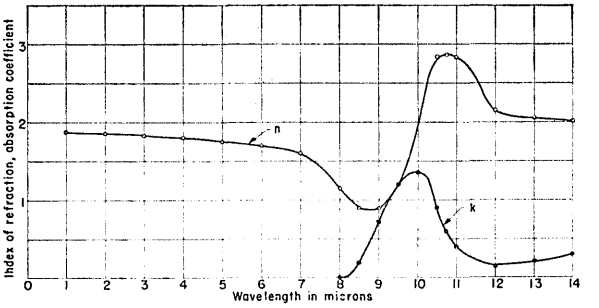

FIG. 5. Index of refraction and absorption coefficient of SiO in the infrared.

invaluable in applications where the value of the refraction index is critical, such as in nonreflecting coatings and multilayer film combinations.

The effect of oxidation on the infrared optical behavior of the films is shown in Fig. 7. The 10-micron absorption peak, characteristic of true SiO, is shifted toward shorter wavelengths and the amount of absorption is increased. Also the extent of the absorbing region is narrowed as would be expected since most of the material is converted from SiO to SiO_2. It should be noted from this figure that similar changes in optical properties result when oxidation is produced either by gettering while the film is being condensed or by prolonged baking in air after the film has been deposited.

The infrared transmittance and reflectance of an SiO_2 film on a rock-salt plate are shown for comparison in Fig. 8. The SiO_2 film was obtained by condensing fumes produced by exposing $SiCl_4$ to moist air, and then baking the film for 8 hours in air at 350°C to remove the strong water absorption band at 3 microns. The similarity between these SiO_2 film curves and those shown in Fig. 7 is evident. By using extreme evaporation conditions ($p \sim 5\times10^{-4}$ mm Hg of oxygen and deposition rate ~1A/sec) films can be prepared with properties almost identical to those of SiO_2. The reflectance of a fused-quartz plate is included in Fig. 8 to show the difference in optical behavior of bulk SiO_2 and thin SiO_2 films.

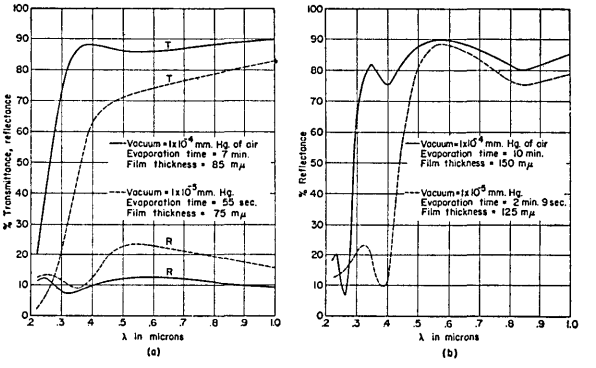

FIG. 6. Influence of the SiO evaporation conditions on the optical behavior of a coated fused-quartz plate (a), and a front surface aluminum mirror (b).

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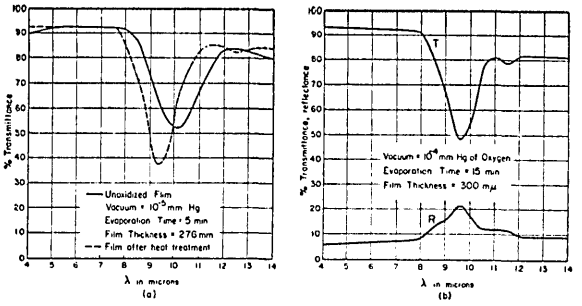

FIG. 7. Effect of oxidation on the infrared behavior of SiO films; oxidation produced by (a) heat treatment in air, (b) slow evaporation in an oxygen atmosphere.

C. Thickness Increase Produced by Oxidizing Films of Silicon Monoxide to Silicon Dioxide

Thin films of silicon monoxide can be oxidized completely to silicon dioxide by heating in air. By measuring the thickness increase, produced by complete oxidation of silicon monoxide films, conclusions on the composition of the untreated film materials can be drawn. If a true silicon monoxide film is oxidized to silicon dioxide, the thickness ratio of the silicon dioxide film to the replaced silicon monoxide film should be

$$\frac{t_{SiO_2}}{t_{SiO}}=\frac{M_{SiO_2}\rho_{SiO}}{M_{SiO}\,\rho_{SiO_2}}=1.35,$$

where M_{SiO_2}, the molecular weight of $SiO_2=30$, M_{SiO}, the molecular weight of $SiO=22$, ρ_{SiO}, the density of $SiO=2.18\pm0.03$,[1] and ρ_{SiO_2}, the density of SiO_2 (fused quartz) $=2.20$. Five silicon monoxide films, ranging in thickness from 750A to 2500A, were deposited onto fused quartz at a vacuum of $\sim1\times10^{-5}$ mm Hg with a deposition rate of 10 to 14A/sec and oxidized completely by heating in air at 700 to 800°C.‡ By measuring the thickness of these five films before and after complete oxidation the average thickness ratio

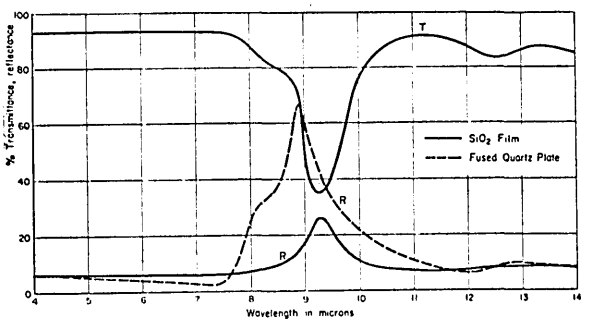

FIG. 8. Infrared transmittance and reflectance of an SiO_2 film on rock salt produced by fuming $SiCl_4$ and baking at 350°C. Dotted line shows the reflectance of a 3 mm thick fused-quartz plate.

‡ The completely oxidized SiO film shows no absorption in the ultraviolet and has the structure of amorphous SiO_2.

was determined to be

$$t_{SiO_2}/t_{SiO}=1.36\pm0.03.$$

The measured ratio value is in good agreement with the calculated one. This may be considered as further proof that silicon monoxide films condensed under the conditions mentioned above consist of true SiO.

While the thickness of a true silicon monoxide film increases by a factor of 1.35 during its oxidation, its optical thickness nt in the visible region remains almost completely constant. This is because of the fact that the ratio of the refractive indexes of silicon monoxide to fused quartz is, in the visible, equal to the factor of thickness increase. Films produced by slow deposition (deposition rate $\lesssim$3A/sec) and at high pressures ($p\sim1\times10^{-4}$ mm Hg of air) show much less thickness increase after complete oxidation than true silicon monoxide films.

D. Effect of Decomposition on the Optical Properties of Silicon Monoxide

Vacuum-deposited films of SiO can be decomposed to $Si+SiO_2$ by heating in high vacuum or in an inert

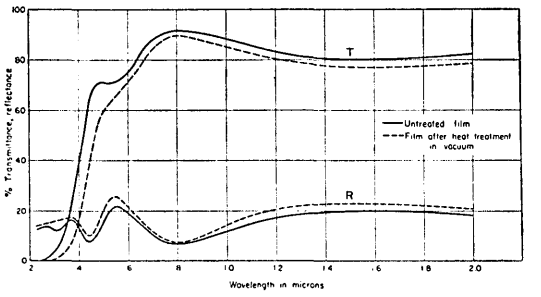

FIG. 9. Effect of decomposition on the optical behavior of SiO; decomposition produced by one hour heat treatment in high vacuum at 850°C.

atmosphere. The decomposition has been demonstrated by electron diffraction studies.[1] Untreated SiO shows a strong halo at $d=3.6$A characteristic for true SiO. After heating the film material in high vacuum at 700°C for 2 hours its electron diffraction pattern consists of several diffuse rings of amorphous Si and amorphous SiO_2. Similar treatments at 800° to 900°C result in a mixture of crystalline Si and amorphous SiO_2.

Figure 9 shows the effect of decomposition on the reflectance and transmittance of a 210-millimicron thick film of SiO in the wavelength region from 0.28 to 2.0 microns. The film was deposited in 3 min at a vacuum of 1×10^{-5} mm Hg on fused quartz and decomposed by heating at 850°C in an oil-free high vacuum of 2×10^{-6} mm Hg. The heat treated decomposed film material shows higher absorption in the ultraviolet and the visible and has a higher index of refraction than the untreated true SiO.

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E. Mirror Protection

Figure 10 shows the infrared reflectance of an untreated aluminum mirror and an aluminum mirror coated with 125 millimicrons of SiO. Also included are the infrared transmittance and reflectance of a filmed rock-salt plate prepared in the same evaporation. In the 10-micron absorption region the thin SiO film reduces the reflectance of aluminum by only 1 percent, but decreases the transmittance of the rock-salt plate by 30 percent, about 18 percent of which is an actual absorption loss. The explanation of why the light reflected from the coated mirror is not absorbed, after presumably passing twice through the thin absorbing film, serves as an excellent illustration of the wave properties of light.

Absorption in a material results from the interaction of the light wave with the atoms and molecules of the material. When light is being transmitted, the traveling

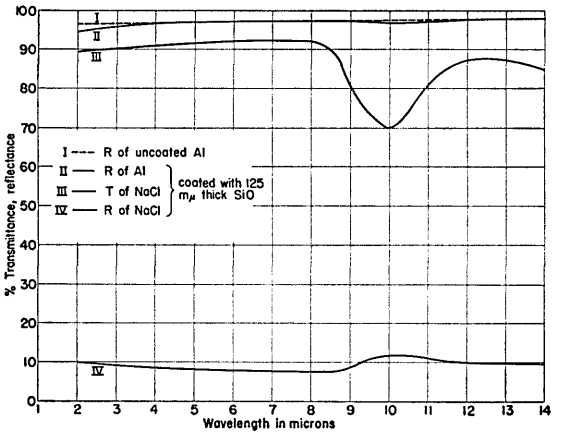

FIG. 10. Comparison of the effect of the same SiO film on the reflectance of an aluminum mirror and the reflectance and transmittance of a rock-salt plate.

wave electric field exists in the material and is absorbed, for example, by exciting molecular resonance vibrations. When the light is reflected a standing wave pattern is set up. If the reflection is from a metal, then an electric field null in the standing wave pattern must exist at the reflecting surface because the metal (assumed to be a perfect conductor) cannot support a tangential electric field at its surface. For the case illustrated in Fig. 10,

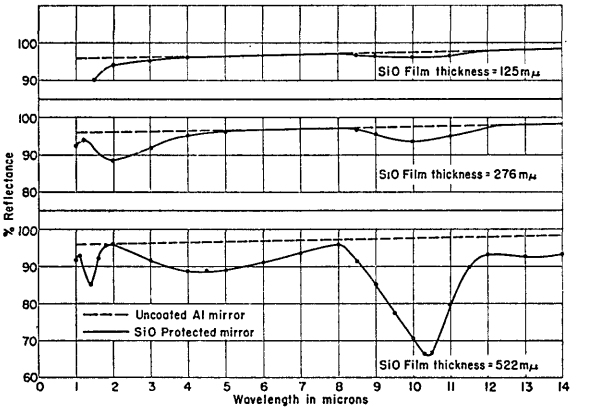

FIG. 11. Infrared reflectance of aluminum mirrors protected with three successively thicker SiO films.

there is an absorbing dielectric film which is only 1/80 of a wavelength thick placed adjacent to the electric field null in the standing wave. The electric field which exists in this small thickness of material adjacent to the null is negligible; therefore, there can be no appreciable absorption in the material.

The amplitude of the electric field increases harmonically with distance from the null at the surface; therefore, the absorption loss in protective coatings should be a strong function of coating thickness. In Fig. 11 the reflectance of three protected mirrors whose coatings successively double in thickness is plotted to illustrate this. The reflection losses at the absorption maximum are approximately in the ratio of 1:4:30 while the ratio of thicknesses is only 1:2:4.

In practice, SiO protective films whose thicknesses range between 100 and 200 millimicrons are sufficient to provide the necessary mechanical and chemical stability. Such films, as indicated, produce no appreciable absorption when the mirror application is in the infrared. In the ultraviolet region the film thicknesses are the same order of magnitude as the wavelength at which absorption occurs; consequently SiO protected mirrors cannot be used in the ultraviolet. However, as previously noted in the discussion of oxidation effects, the absorption can be shifted by partial oxidation, and protected mirrors with good reflecting properties down to 300 millimicrons can be prepared.

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