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IMPROVED DIELECTRIC FILMS FOR MULTILAYER COATINGS AND MIRROR PROTECTION

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Résumé. — Ce mémoire contient des données sur les propriétés optiques de couches d’oxydes de silicium, d’aluminium, de thorium et de zircone préparées par évaporation. Le domaine de longueur d’onde s’étend de 0.2 μ à 1.6 μ. Les couches étaient préparées, soit par chauffage direct dans l’oxygène à faible pression, soit par bombardement électronique. On décrit quelques applications : protection des miroirs, surfaces antiréfléchissantes, filtres par réflexion, et surfaces servant au contrôle de la température des satellites.

Abstract. — This paper presents data on the optical properties of evaporated films of silicon oxide, aluminium oxide, thorium oxide, and zirconium oxide in the wavelength region from 0.2 μ to 1.6 μ. The films were prepared by direct heating both in vacuum and in the presence of oxygen, and by electron bombardment. Some of their more important applications such as: protected front surface mirrors, antireflection coatings, reflection filters, and coatings for controlling the temperature of satellites in outer space, are described.

I. Introduction. — For a long time, the designer of multilayer antireflection coatings and protected front surface mirrors was seriously hampered by the fact that the number of dielectric materials suitable for producing durable and nonabsorbing films by direct evaporation in high vacuum was quite restricted. Only recently, new deposition techniques and treatments, such as evaporation by electron bombardment, deposition in the presence of oxygen, and exposure to ultraviolet radiation, have greatly increased the number of oxides that can now be deposited in the form of nonabsorbing coatings. These new techniques have been especially suitable for producing durable optical coatings of Si₂O₃, SiO₂, Al₂O₃, ThO₂, and ZrO₂.

It is the purpose of this paper to present data on the preparation and optical properties of these oxide films and to discuss some of their applications, such as the preparation of well protected front surface mirrors with high reflectance in the ultraviolet, multilayer antireflection coatings, and surface films for controlling the temperature of satellites in outer space.

II. Experimental techniques. — The evaporations were performed in a 60 cm vacuum system in which film depositions could be monitored by reflectance measurements with monochromatic light. Polished plates of glass, fused quartz and sapphire were used as substrates. They were mounted about 45 cm above the evaporation sources, and could be cleaned by a high-voltage dc glow discharge using up to 5 kV and 100 ma, and could be heated up to 350 °C. A removable shutter was placed close to the substrate plates to avoid their contamination during the outgasing of the evaporation sources and charges. Silicon monoxide was evaporated from a tantalum container by direct heating. A high-powered electron gun capable of applying up to 20 kV and 250 ma was used for evaporating SiO₂, Al₂O₃, ThO₂, and ZrO₂. The oxides to be evaporated by electron bombardment were placed into a dimple of a heavy copper block. To assure high and rather constant evaporation rates, and to avoid overheating and decomposing the oxides, an electron beam of at least 1.5 cm diameter was used. With this technique, films of SiO₂ and Al₂O₃ produced at deposition rates of about 400 Å/min and at a distance 45 cm from the evaporation source, showed no absorbance in the visible and ultraviolet. This is not true for films produced with a highly focussed electron beam.

The reflectance and transmittance of films deposited under various conditions onto transparent substrates and onto evaporated aluminum were measured from 2 000 Å to 15 μ with Perkin Elmer and Beckman instruments. The refractive indices of nonabsorbing films were computed from the measured reflectance values at the quarter-wavelength positions. Additional values for the film indices were determined from the true interferometrically determined film thicknesses and the wavelength positions of reflectance maxima and minima.

III. Results. — 1. Films produced by evaporation of SiO. — Thin films produced by high vacuum evaporation of silicon monoxide are, today, the most frequently used protective layers for evaporated aluminum mirrors. However the composition and optical properties of such protective films and the reflectance characteristics of protected aluminum mirrors depend strongly upon the conditions under which SiO is evaporated [1-3]. High deposition rate at low pressure results in films of true SiO which show rather strong absorbance in the ultraviolet and shorter wavelength...
region of the visible. Coatings prepared at a low deposition rate and rather high pressure of oxygen are strongly oxidized and show a large shift of the absorption edge toward shorter wavelength, negligible absorptance in the visible and near ultraviolet, and lower index of refraction. Aluminum mirrors that are to be used in the visible and near ultraviolet should therefore be protected with a strongly oxidized film rather than with one of true SiO. Below $\lambda = 300 \mu\text{m}$, strongly oxidized silicon oxide films still show rather strong absorptance which increases with decreasing wavelength. This has for a long period of time limited their usefulness as protective layers for aluminum mirrors. Recently it has been shown that exposure to the ultraviolet radiation of a quartz mercury burner completely eliminates the undesired ultraviolet absorptance of strongly oxidized silicon oxide films and thus makes it possible to produce well-protected aluminum mirrors with high reflectance throughout the far ultraviolet [7]. Figure 1 shows the effect of SiO evaporation conditions and ultraviolet irradiation on the visible and ultraviolet reflectance of silicon oxide protected aluminum mirrors. Protective coatings effectively $\lambda/2$ thick at 550 $\mu\text{m}$. Irradiation performed with 435 watt quartz mercury burner at a distance of 20 cm.

Strongly oxidized films of silicon oxide have also been deposited on ultraviolet transparent fused quartz and sapphire and measured in transmittance and reflectance before and after ultraviolet irradiation. Their initially rather high ultraviolet absorptance could be completely eliminated and their refractive indices were greatly decreased by the ultraviolet treatment. Figure 2 shows the refractive index of a silicon oxide film, produced by evaporating SiO slowly in the presence of oxygen, before and after ultraviolet irradiation from 0.2 to 1.6 $\mu\text{m}$. A film prepared under the described conditions consists predominately of $\text{Si}_2\text{O}_3$ [4-6,8] and shows an initial refractive index of 1.57 at $\lambda = 600 \mu\text{m}$. After 5 hours of ultraviolet irradiation, its refractive index is decreased to 1.48 at the same wavelength, which brings it near to that of fused quartz. However, measurements of the infrared absorption spectra of such films have led to the conclusion that 5 hours of ultraviolet treatment does not convert $\text{Si}_2\text{O}_3$ into $\text{SiO}_2$.

### 2. $\text{SiO}_2$ Films Produced by Electron Bombardment

Undecomposed films of $\text{SiO}_2$ can be produced by electron bombardment. Figure 3 shows the refractive index of evaporated $\text{SiO}_2$ films produced by electron bombardment, in the wavelength region from 0.2 to 1.6 $\mu\text{m}$.

![Fig. 1.](image1.png)  
**Fig. 1.** — Effect of SiO evaporation conditions and ultraviolet irradiation on the visible and ultraviolet reflectance of silicon oxide protected aluminum mirrors. Protective coatings effectively $\lambda/2$ thick at 550 $\mu\text{m}$. Irradiation performed with 435 watt quartz mercury burner at a distance of 20 cm.

![Fig. 2.](image2.png)  
**Fig. 2.** — Refractive index of a silicon oxide film produced by evaporating SiO slowly in the presence of O$_2$, before and after ultraviolet irradiation, from $\lambda : 0.2$ to $1.6 \mu\text{m}$. Deposition rate $3 \text{Å/sec}$ at $8 \times 10^{-5} \text{torr}$.

![Fig. 3.](image3.png)  
**Fig. 3.** — Refractive index of evaporated $\text{SiO}_2$ produced by electron bombardment, in the wavelength region from 0.2 to 1.6 $\mu\text{m}$.
obtained by evaporating quartz glass with an electron gun. If properly evaporated, such films show no absorptance in the ultraviolet and visible, and have a refractive index which is identical to that of fused quartz. Figure 3 shows the dispersion curve of SiO₂ films produced by electron bombardment in the wavelength region from 0.2 μ to 1.6 μ. The measurements were made on films of various thicknesses deposited at rates of 400 to 800 Å/min at a distance of about 45 cm. They show no interference effects when evaporated onto quartz glass since they have the same index of refraction. Such films are especially suitable for producing chemically and mechanically durable protective layers for front surface mirrors. The ultraviolet and visible reflectance of aluminum with and without a 7 800 Å thick protective film of SiO₂ is shown in figure 4. Even in the far ultraviolet the protected mirror shows, at the interference maxima, slightly higher reflectance values than the unprotected one, which proves that the SiO₂ film is free of absorptance in the wavelength region shown. Much thinner protective layers of SiO₂ should be used of course for producing the most efficient front surface mirrors for the visible and ultraviolet.

3. Aluminum oxide films produced by electron bombardment. — Another material which should be useful for producing optical coatings is aluminum oxide because it is both extremely hard and transparent in the far ultraviolet. Aluminum oxide (Al₂O₃) can be evaporated from tungsten heaters but the resulting films are slightly decomposed, due to reduction by tungsten, and show some absorptance. Decomposition, and therefore absorption, can be avoided by using electron bombardment for the evaporation of aluminum oxide. With this technique extremely hard and durable Al₂O₃ films, up to several micrometer in thickness, can easily be prepared which show no absorptance in the visible and ultraviolet. The refractive indices of aluminum oxide films evaporated by electron bombardment onto substrates at 40 °C and 300 °C are shown in figure 5 for the wavelength region from 0.2 μ to 1.6 μ. The refractive indices of the films produced at 300 °C are slightly higher than those of the films prepared at 40 °C. In the visible at λ = 500 μm an increase of the substrate temperature from 40 °C to 300 °C causes a rise in the refractive index from 1.60 to 1.63. These values are considerably smaller than those of crystalline γ-Al₂O₃ films produced by reactive sputtering onto glass at higher substrate temperatures [9]. This is due to the fact that the evaporated films condensed on substrates of 40 °C and 300 °C are amorphous. Their indices agree well therefore with those of amorphous Al₂O₃ films prepared by anodic oxidation [10], and deposition from organic solutions [11].

Because of their hardness and excellent adherence, evaporated Al₂O₃ films are very suitable as protective layers for aluminum front surface mirrors. Figure 6 shows the visible and ultraviolet reflectance of evaporated aluminum with and without Al₂O₃ protective films of two different thicknesses. To obtain highest reflectance
in the ultraviolet, an oxide thickness of 740 Å was used, and to produce highest reflectance in the visible the thickness of the oxide film applied was 1740 Å. This makes the Al₂O₃ films effectively one half wavelength thick at \( \lambda = 250 \mu \) at \( \lambda = 550 \mu \), respectively. It can be seen that the Al₂O₃ films do not exhibit any noticeable absorptance in the wavelength region shown.

Al₂O₃-protected aluminum mirrors show very good abrasion and scratch resistance. They cannot be damaged by rubbing with rough linen and can be repeatedly cleaned with water and detergent without changing their reflectance. They are, however, more sensitive to salt spray and boiling water than silicon oxide protected mirrors.

Figure 7 demonstrates the use of Al₂O₃ films in multilayer anti-reflection coatings for glass. It shows the visible reflectance of glass \((n_e = 1.51)\) with and without a three-layer antireflection coating \((\lambda/4 - \lambda/2 - \lambda/4)\) of \(\text{Al}_2\text{O}_3 + \text{ZrO}_2 + \text{MgF}_2\), from \(\lambda = 400\) to 700 μm.

Evaporated Al₂O₃ can also be used in combination with films of rhodium for producing mirror coatings with low visible and high infrared reflectance similar to the ones described by Hass et al. [12]. This new type of “dark mirror” consisting of Rh (opaque) — Al₂O₃ — Rh (semi-transparent) — Al₂O₃ is very temperature resistant and is, therefore, especially suitable for use in solar energy converters. The Rh films used in this combination should also be evaporated by electron bombardment.

4. Thorium dioxide films produced by electron bombardment. — Films of thorium dioxide (ThO₂) are of special interest since they are transparent throughout most of the ultraviolet region and have a rather high index of refraction. ThO₂ films have, therefore, been used in combination with low-index films of SiO₂ for producing multilayer interference filters, [13] and multilayer polarizers [14] for the ultraviolet region. The films for these applications were prepared by deposition from organic solutions. Using electron bombardment, stable and nonabsorbing coatings of ThO₂ can also be prepared by high vacuum evaporation. Figure 8 shows the dispersion curve of ThO₂ films evaporated onto fused quartz at close to room temperature in the wavelength region from 0.2 μ to 1.6 μ. The refractive indices of evaporated ThO₂ are considerably lower than those prepared from organic solutions by Schroeder [11]. Their index in the ultraviolet is high enough however to use them in combination with evaporated low-index films of SiO₂ for enhancing the reflectance of aluminum in this spectral region. The ultraviolet reflectance of aluminum coated with a reflectance-increasing film pair of SiO₂ + ThO₂ is shown in figure 9. Both dielectric films are effectively one quarter wavelength thick at \( \lambda = 290 \mu \), and result in a maximum reflectance of more than 95%. The region of high reflectance can be shifted to shorter and longer wavelengths and its maximum can be increased by adding additional film pairs of SiO₂ and ThO₂.
5. Coatings for controlling the temperature of satellites. — Evaporated films of aluminum plus silicon oxide have played an important role as surface coatings for controlling the temperature of satellites in outer space [15]. The temperature control of an orbiting satellite with small internal power dissipation is established by arranging for the solar energy absorbed to be balanced by the thermal radiant energy emitted by the surface at the temperature desired for the payload. For a given orbit, therefore, the crucial parameter is the ratio of the effective solar absorptance, $a$, of the surface to its hemispherical emittance, $e$. For spherical satellites this ratio of $a/e$ should be about 1.2 for maintaining the satellite at close to room temperature. Highly polished metal surfaces have $a/e$ values of 4 to 10 which would result in very hot satellites and failure of their instruments. By using aluminum in combination with surface films that are nonabsorbing in the solar region but strongly absorbing in the far infrared, surfaces with a wide range of $a/e$ values can easily be prepared.

If evaporated aluminum is coated with a non-absorbing surface film with an index of 1.5 to 1.6, and a thickness greater than 0.3 μ, its solar absorptance becomes almost independent of the surface film thickness and assumes a value of 11.5 % to 12.5 %. If the surface film has strong infrared absorption bands the thermal emittance of the overcoated aluminum increases greatly with increasing thickness of the surface film. By using evaporated silicon oxide or aluminum oxide coatings of various thicknesses on top of opaque aluminum, surfaces with any desired $a/e$ ratio from about 5 to 0.25 can be prepared. Figure 10 shows the infrared reflectance of aluminum coated 0.5, 1.0, and 1.5 μ thick films of $\text{Al}_2\text{O}_3$. It can be seen that increasing the $\text{Al}_2\text{O}_3$ thickness decreases greatly the infrared reflectance of $\text{Al}_2\text{O}_3$ coated aluminum and thus increases its thermal emittance without changing its solar absorptance. Up to now, more than thirty satellites of different shapes and sizes have been coated with aluminum and silicon oxide, and the coatings have been completely successful in stabilizing their temperature to the desired range of 15₀ to 35 °C. The same results can be obtained with coatings of $\text{Al} + \text{Al}_2\text{O}_3$.

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