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FURTHER OPTION FOR SOLAR CONCENTRATORS: ALUMINUM FIRST SURFACE MIRRORS

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Abstract—The research and development of aluminum first surface solar mirrors is presented. Two protection films for the aluminum layer are discussed: Si_2O_3 and SiO_2. Two electron guns (e-gun) are used to manufacture aluminum first surface solar mirrors. One, for aluminum evaporation, eliminates or minimizes pinholes observed when aluminum is evaporated with tungsten filaments. The other e-gun allows the evaporation of SiO and SiO_2 without the mirror contamination previously seen due to the air when the chamber was opened. Better adherence between the aluminum film and the Si_2O_3 or SiO_2 is obtained due the use of two electron guns that does not permit the chamber to open. Si_2O_3 is a material obtained by oxidation of SiO by admitting some oxygen into the evaporation chamber (10^{-4} Torr). The optimum thickness of the aluminum layer was 1000 Å or higher, about 2500 Å for the Si_2O_3, and 3200 Å for the SiO_2. The specular reflectance of these mirrors is about 0.89. These mirrors were tested in the environmental chamber for accelerated weathering without any important degradation, making them another option for solar concentrators in solar energy applications.

1. INTRODUCTION

The long-term degradation of solar mirrors can range from a negligible destruction of the mirror to a total one, depending on the outdoor environment. For this reason, the study of several options for solar reflectors is important. The most common option has been silver second surface mirrors. The substrates are generally glass, or transparent sheets of plastic, where silver or aluminum is deposited to form a second surface mirror protected against the environment. However, there are some other alternatives, such as the sol-gel mirrors and the first surface mirrors, as discussed by Reed and Ashley (1988), and Ashley et al. (1988).

In first surface mirrors, the substrates can be glass, metals, or plastic where silver or aluminum is first deposited and later a transparent thin film is deposited over the reflecting film as a "front surface." Usually, the silver mirrors have a higher reflectance than aluminum mirrors, however, four layers are needed to obtain a good silver mirror, as developed by Hass et al. (1982) and Bacuchi (1983), instead of two layers as needed with the aluminum mirrors (aluminum and transparent front surface films). Furthermore, the corrosion problems in aluminum first surface mirrors are less serious than in silver mirrors because the adherence to the glass in aluminum mirrors is better and sulfide tarnishing does not exist. In order to estimate if such mirrors are a good option for solar energy applications and can achieve routine production of long life mirrors, it is necessary to know how they work under severe environmental conditions.

In this study, Al and SiO or SiO_2 were employed as reflective and protective layer materials in succession. Aluminum has a high reflectance of 0.90–0.92 (M = 1.5), as measured by Richmond (1984) and by Griffin (1980), it adheres well to glass surfaces, and does not tarnish in normal air, as discussed by Hass et al. (1982). All silicon oxides, SiO, SiO_2, and Si_2O_3, exhibit stronger absorption bands in the important 9–12 μm atmosphere window, as pointed by Hass et al. (1982). However, for the terrestrial solar spectrum region (0.3–2.5 μm), the absorption in the atmosphere window does not obviously influence the transmittance of the film. Besides, the Si_2O_3 and SiO_2 films have a very good affinity to the Al-film, therefore, both films make excellent protective layers of first surface mirrors. When SiO is evaporated in the presence of oxygen at low rates, the Si_2O_3 is the most important composition, however, there is also the presence of SiO_2 and SiO, as discussed by Almanza et al. (1992a). For this reason, the stoichiometry of the film is expressed by Si_yO_x in this paper.

In this paper the advances and final results for the two options, Si_2O_3 and SiO_2 in aluminum first surface mirrors are presented. Some papers about the development of these reflectors and their advantages have previously been published by Almanza et al. (1991, 1992a, and 1992b).

2. EXPERIMENTAL EQUIPMENT

A first surface mirror was built by evaporation of a thin aluminum film over a substrate, which in this case was a sheet of float soda-lime silica glass. The aluminum film is usually protected against abrasion and corrosion by a transparent thin layer that can be SiO, SiO_2, Si_2O_3, plastic, silicon resins, etc.

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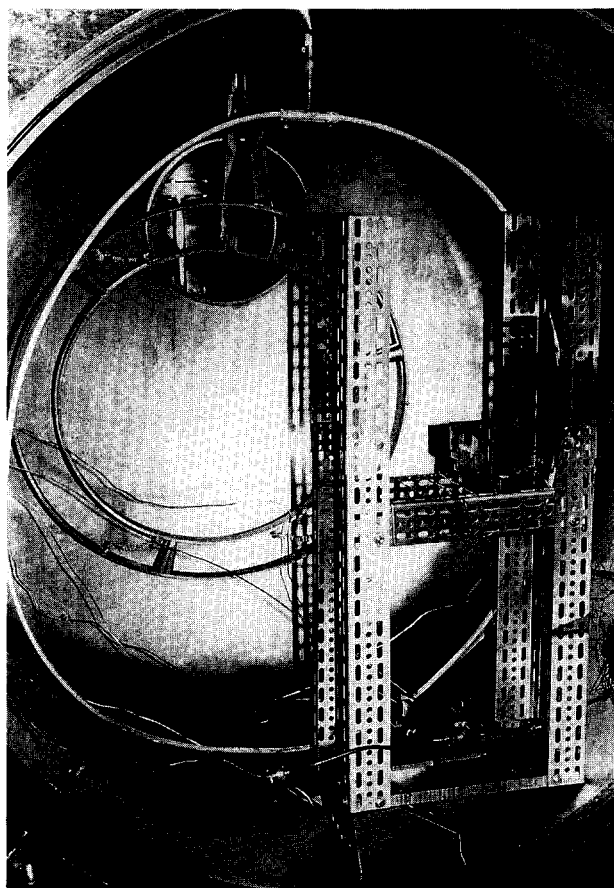** Visiting professor from Shanghai Institute of Ceramics, Chinese Academy of Sciences.

Fig. 1. Two e-guns and their arrangement inside the evaporator chamber.

Almanza et al. (1992a), in a preliminary stage, used a tungsten filament to evaporate the aluminum, but some pinholes on the mirror surface were observed. These holes on the mirror surface were the main cause of corrosion in outdoor tests. In a second stage, Almanza et al. (1991, 1992b) built an e-gun in order to eliminate the pinholes during the aluminum evaporation, but one problem emerged. It was necessary to open the evaporator in order to introduce a crucible with SiO or SiO_2 for the protection layer.

Along this last line, some improvements were made. The most important one was that two e-guns were installed in the evaporator. With two e-guns (Fig. 1), it was possible to evaporate Al as well as the dielectrics SiO or SiO_2 without opening the system and to deposit the dielectrics after the Al film without any contamination. In this way the aluminum first surface mirror was formed with a better adherence between the aluminum and the Si_yO_x or SiO_2. In order to produce sufficient evaporation from the crucibles and to avoid decomposing dielectrics, both water-cooled e-guns were designed with a beam area of about 1 cm^2. Figure 1 shows the location of both e-guns with their crucibles and glass samples (located in the horizontal beams) within the vacuum chamber.

Two boat-like crucibles can be placed on the guns. One crucible made of BN is used only for Al evapora-

tion, whereas the other, a graphite one, is used for SiO or SiO_2 evaporation. These two kinds of crucibles have been shown to be stable for Al and SiO or SiO_2 evaporation, respectively. BN has a good wetting to Al, and the graphite crucible does not contaminate the protection films. Two electromagnetically controlled shutters are placed over the guns, which allow or prevent the evaporants to be deposited on the glass sheet.

A circular aluminum glow discharge cathode, which consists of a 90 cm diameter ring made of 10 mm diameter aluminum tubing, is suspended in the centre of the 1.5 m^3 evaporator, near the glass sheets, and insulated from the grounded evaporator wall. The cathode is connected to a DC high-voltage power supply capable of furnishing 5 KV and 1000 mA. The sensor (quartz crystal) for thickness measurements and deposition rate of the films is installed on the frame at the same height as the glass sheets.

3. PREPARATION PROCESSES FOR THE MIRRORS

3.1 Cleaning the glass substrate

Substrate cleaning is a very important step in the preparation for deposition of any film or coating in order to get a good adherence. The process of substrate cleaning requires that bonds between contamination

Table 1. Reflectance at different aluminum deposition rates

Sample	Film Thickness (Å) Al	Film Thickness (Å) Si$_y$O$_x$	Rate (Å/s)	ρ_s
04-29-2	4000	2000	8.0	0.864
07-08-2	1092	2000	7.4	0.872
04-27-1	2016	2000	7.3	0.841
05-04-1	2000	2500	7.0	0.866
03-30-2	1313	2500	2.9	0.809
02-20-1	1070	2000	1.8	0.805
04-20-1	2000	2000	1.5	0.811
04-20-1	2000	2000	1.5	0.803

molecules, as well as between the contaminant and the substrate be broken, as discussed by Brown (1970). Thus, the final choice of cleaning techniques depends much on the substrate materials, the type of contaminants, and the degree of cleanliness.

Cleaning the glass substrate is essential to enhance the adhesion between films and glass, and to minimize corrosion of the first surface mirrors. The glass sheet must be cleaned to remove dirt, grease, gel, any oxide layer, etc. before being placed inside the evaporator. Any trace of contamination on the glass surface can cause film defects. In this experiment, commercial float soda-lime glasses were used as the substrates. An aqueous acid solution and glow discharge were employed as cleaning techniques. It is not possible to predict a product's useful lifetime if there is previous contamination.

The cleaning procedures were as follows:

1. A glass sheet with dimensions 100 × 40 × 3 mm was scrubbed with clean soft cloth dipped in detergent solution; it was rinsed with running water until no detergent solution film was left on the surfaces.
2. After this preliminary cleaning, the glass sheets were immersed in a chromic sulphuric acid solution for half an hour at a temperature of 70–80°C.
3. The glass sheets were slowly withdrawn from the solution, then rinsed with water, and wiped with a cloth until no residual solution was left on the glass surfaces. In order to dry some of the water film that remained on the glass sheets, they were placed vertically in air or inside an oven at a temperature lower than 100°C.
4. As a final step, the glass sheets were dipped into a distilled water container, and afterwards, into a water-free isopropylic alcohol container. Finally, they were placed vertically inside the oven at 90–110°C temperature for 20–30 min.

During the cleaning of glass substrates, good wetting between glass surfaces and water is required. By this means it is possible to examine if the glass substrate is well cleaned. This is called "the water-break-test" as suggested by Brown (1970).

3.2 Deposition of Al and Si$_y$O$_x$ films

Completely cleaned glass sheets were placed inside the vacuum chamber and mounted on the sample-frame at a height of 40 cm above the evaporation sources. They were distributed in an area of 20 × 15 cm so that the vapor incidence angle was not greater than 30°. In our study, 99.999% high purity Al was used as the starting material of the reflecting film. SiO or SiO$_2$ (quartz) was the second evaporating material for the protective layer over the reflecting film. Their purities were 99.9% and 99.98%, respectively.

A glow discharge was used as an in situ cleaning technique for the glass substrate. During the glow discharge, oxygen was introduced in order to increase the adhesion between the Al film and the glass substrate.

After the glow discharge, a reflecting film of Al approximately 1000Å thick was deposited on the glass surface at a pressure of about 5×10^{-5} Torr. Oxygen was again introduced into the evaporator up to a pressure of 8–9×10^{-5} to 1×10^{-4} Torr for Si$_y$O$_x$ film reactive evaporation, as presented by Hass et al. (1982) and by Glang (1970). A Si$_y$O$_x$ layer about 2500Å thick was produced at a mean rate of 1–3 Å/sec. If SiO$_2$ film was the protective layer instead of Si$_y$O$_x$, SiO$_2$ film about 3200Å thick was deposited at
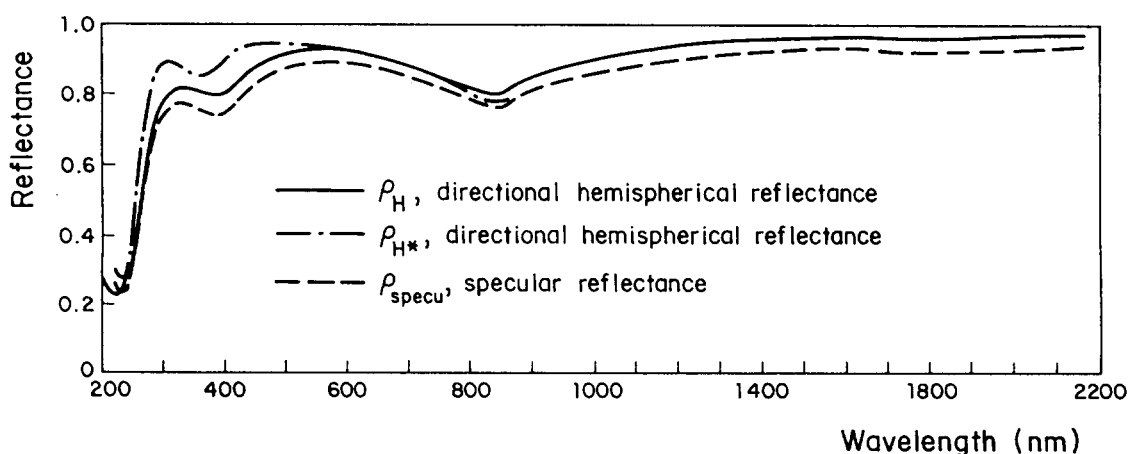

Fig. 2. Spectral reflectance of Al-Si$_y$O$_x$ first surface solar mirror.

Table 2. Parameters and values considered for accelerated ageing tests

Humidity	Room temperature and 100% relative humidity 50°C and ~60% relative humidity
Thermal cycling	50°C for 1 h Cooled down to RT and keep for 1 h. Dip to liquid nitrogen (−195°C) for 20 minutes. Let reach room temperature and keep for 1 hour. At the end of this, begin a new cycle.
Temperature test	70°C
Salt water immersion	5% (w/w) solution of NaCl, room temperature
Exposure to moist sulfur dioxide	Room temperature
Abrasion test	Dry and wet abrasion

a mean rate of 400Å/min without introducing oxygen, as discussed by Ritter (1975).

In order to produce a low absorption Si_2O_3 layer in the solar spectrum region, low deposition rate and high oxygen pressure were employed. These were advantageous to the change from SiO to Si_2O_3, though some SiO and SiO_2 also remained. Although the rate of 400Å/min for SiO_2 is recommended, it is difficult to keep this rate because it is out of range of our thickness sensor. For this reason, the evaporation was carried out at ~150Å/min.

4. PROPERTIES OF THE MIRRORS

4.1 Measurements of optical properties

For first surface mirrors in solar energy applications, the reflectance ρ_s is the most important optical property that determines their efficiency in service, and is one criterion by which degradation is evaluated. Two measuring methods for ρ_s of the mirrors in this study were employed: total specular reflectance measurement and spectral reflectance measurement.

4.1.1 *Total specular reflectance measurement.* The total specular reflectance was measured with a solar spectrum reflectometer (SSR) from Devices & Services Co. Al films with different thicknesses and deposition rates were prepared in order to find the relationship between thicknesses, deposition rates of the Al film, and reflectance. Table 1 gives the measurement results. As can be seen in this table, the rate of evapo-

ration is very important. This is in accordance with Hass *et al.* (1982) and Pulker (1984).

4.1.2 *Spectral reflectance measurements.* Another technique for determining ρ_s was by means of spectral reflectance measurements as suggested by Hass *et al.* (1982), Richmond (1984), Edwards *et al.* (1961) and ASTM (1983). These measurements were performed with Cary 2300 and Shimatzu spectrophotometers. Spectral reflectance measurements can provide solar reflectance with high accuracy, and more detailed information on materials or films than the measurement of total specular reflectance. For example, the reflectance of the mirrors as a function of the wavelength can be clearly observed from spectral reflectance curves.

Figure 2 is the spectral reflectance of some mirrors. ρ_H and ρ_{H*} are the directional hemispherical reflectance measured with $BaSO_4$ as the reference standard using Cary 2300 and Shimatzu Spectrophotometers separately. ρ_{specu} is the specular reflectance measured with the Integrating Sphere attachment of the Cary 2300 Spectrophotometer.

4.2 Adhesion between film and glass substrate

Debonding of film and substrate is a common failure of mirrors. It can cause severe degradation of the mirrors from visible surface defects to nearly complete destruction of the film. In order to examine bonding between films and between the film and the glass substrate, two tests have been conducted. The first test

Table 3. Reflectance after 100% RH at room temperature

Sample	Thickness (Å)		Reflectance ρ_3					Comments
	Al	Si_yO_x	Previous	Exposure time: (weeks)				
				1	2	3	4	
3-11-2	1340	2230	0.850	0.862	0.859	0.859	0.855	very small holes
4-1-1	1500	2522	0.843	0.847	0.845	0.844	0.844	very small holes
4-8-2	1517	748	0.843	0.832	0.822	0.818	0.822	very small holes
4-20-1	2000	2200	0.811	0.826	0.820	0.820	0.820	very small holes
4-27-2	2000	2000	0.840	0.854	0.851	0.852	0.845	
4-29-3	4000	2500	0.864	0.875	0.870	0.870	0.868	
5-4-3	2000	2500	0.866	0.877	0.877	0.879	0.873	

Table 4. Reflectance after 100% RH exposure at room temperature

Sample	Film thickness (Å)		Reflectance ρ_s			
	Al	Si_yO_x	Previous	Exposure time: (weeks)		
				1	2	3
10-07-1	1257	2850	0.888	0.887	0.887	0.887
10-01-1	980	1557	0.852	0.853	0.852	0.853
09-29-2	1413	1552	0.850	0.850	0.850	0.851
09-24-1	1454	2600	0.879	0.880	0.879	0.879
09-18-1	1225	2534	0.886	0.887	0.886	0.887
09-14-2	1247	2361	0.884	0.884	0.882	0.884
09-08-2	1012	2053	0.868	0.868	0.866	0.868
07-16-2	1000	2200	0.875	0.876	0.873	0.875
07-08-1	1092	2000	0.871	0.873	0.870	0.873

Table 6. Reflectance after thermal cycling

Sample	Thickness (Å)		Reflectance ρ_s		Comments
	Al	Si_yO_x	Previous	After 5 cycles	
10-07-3	1257	2850	0.884	0.880	glass was cracked
09-24-2	1454	2600	0.877	0.874	
09-18-2	1225	2534	0.885		glass was cracked
08-26-3	1000	2300	0.886	0.883	
07-16-1	1000	2200	0.878	0.878	

was the tape adhesion method as proposed by Campbell (1970). This consists of pressing a piece of adhesive tape to the film. When the tape is pulled off, the film is either wholly removed, partially removed, or left behind on the substrate. In the second test, the mirror is submerged into liquid nitrogen for 10 min, then extracted and its temperature allowed to rise to room temperature. This process is repeated more than 15 times. No change in appearance or mechanical properties of the mirror was observed after the above two tests. These tests indicated that the bonds between Al and protective films and between Al film and glass substrate were very strong. It can be predicted that the mirror will conserve good adhesion for a long time even in outdoor weathering conditions.

When only one e-gun was used, a poor adhesion as a whole between the Si_yO_x and the Al films was observed. This phenomenon was attributed to the influence of air on the aluminum film when the evaporator was opened in order to recharge or replace the SiO. With two e-guns and without opening the vacuum chamber, the problem was eliminated.

5. ACCELERATED AGEING TESTS

Solar mirrors play an important role in various solar thermal technology applications. Mirrors having high performance and long service life are required to keep the cost of solar energy competitive with fossil fuel. However, under outdoor weathering conditions, degradation of solar mirrors to a certain extent is almost unavoidable. Therefore, environment ageing tests are necessary to examine the properties of such mirrors and predict their service life.

Two approaches can be applied to conduct environment ageing tests and study the degradation of solar mirrors. They are referred to as outdoor natural weathering exposure and accelerated environment ageing tests. The former, real environmental ageing exposure is more reliable, but quite difficult because of time consumption and dissimilar conditions among different test locations. Therefore, accelerated environment ageing tests in the laboratory are often employed to examine the performance of solar materials, by means of simulated artificial environment conditions.

In this study, the main objectives are to examine properties of $Al-Si_yO_x$ first surface mirrors and assess the effect of a Si_yO_x (or SiO_2) protection layer against corrosion. The degradation of the tested mirror samples is estimated by changes in appearance and specular reflectance. Before each test, the specular reflectance of the mirror was measured and later at regular intervals.

On the basis of our experience and available literature (Masterson et al., 1983; National Standards for Optical Parts, 1978; Dennis and McGee, 1980), accelerated ageing tests listed on Table 2 were conducted. Some of the more representative experimental results have been listed in Tables 3, 4, 5, 6, 7, 8, 9, 10, and 11.

Humidity tests have been carried out three times. Two test were at room temperature and 100% relative humidity (RH); the other test was under 50°C and

Table 5. Reflectance after 60% RH at 50°C exposure

Sample	Film thickness (Å)		Reflectance ρ_s		
	Al	Si_yO_x	Previous	Exposure time: (weeks)	
				1	2
10-07-1	1257	2850	0.887	0.888	0.887
10-01-1	980	1557	0.853	0.853	0.853
09-29-2	1413	1552	0.851	0.851	0.850
09-24-1	1454	2600	0.879	0.879	0.879
09-18-1	1225	2534	0.887	0.887	0.886
09-14-2	1247	2361	0.884	0.884	0.884
09-08-2	1012	2053	0.868	0.867	0.867
07-16-2	1000	2200	0.875	0.874	0.867
07-08-1	1092	2000	0.873	0.871	0.872

Table 7. Reflectance after 70°C exposure

Sample	Thickness (Å)		Reflectance ρ_s			
	Al	Si_yO_x	Previous	Exposure time		
				24 h	48 h	72 h
09-29-3	1413	1552	0.846	0.847	0.848	0.847
09-22-3	1208	2500	0.868	0.869	0.867	0.866
09-14-1	1247	2361	0.885	0.886	0.885	0.885
07-01-2	1000	2000	0.865	0.864	0.863	0.863

Table 8. Reflectance after sulphur dioxide atmosphere exposure

Sample	Thickness (Å)		Reflectance ρ_s							Comments
	Al	Si$_y$O$_x$	Previous	Exposure time						
				1 h	3 h	6 h	12 h	24 h	48 h	
09-29-1	1413	1552	0.852	0.853	0.853	0.852	0.852	0.848	0.830	
09-24-3	1453	2600	0.874	0.873	0.873	0.874	0.874	0.872	0.864	many small holes
09-18-3	1225	2534	0.881	0.881	0.880	0.881	0.880	0.881	0.881	
08-20-1	1167	2015	0.881	0.880	0.880	0.880	0.879	0.880	0.879	
07-08-2	1092	2000	0.872	0.872	0.873	0.872	0.872	0.873	0.872	

~60% RH. The experimental results have been listed in Tables 3, 4, and 5.

On certain mirror surfaces, transparent spots appeared early in the humidity test and remained unchanged in size thereafter. It is assumed that these spots consisted of alumina formed as a result of pinhole defects in the Si$_y$O$_x$ film, where the Al film would be exposed to water vapor during the test, causing its oxidation. The formation of Al$_2$O$_3 \cdot$ H$_2$O would then ensue which would block and seal the original defect preventing the Al film around the holes from further oxidation, thus limiting the size of the spots.

According to the results in humidity tests (see Table 3), sample 4-8-2 showed a severe drop in reflectance. The reason was that the Si$_y$O$_x$ layer was too thin to protect the Al reflecting film.

Additional mirrors with thicker films were manufactured. These were subjected to two humidity tests. First, the samples listed in Table 4 were tested at room temperature and 100% RH environments for 3 weeks. After that, they were exposed to 50°C and ~60% RH for two weeks. The experimental parameters and results are summarized in Tables 4 and 5. Tables 4 and 5 show better experimental results than Table 3. No obvious degradation of performance occurred.

After every thermal cycle, the surfaces of tested mirrors were carefully checked to determine if any damage, crack, or exfoliation of the films took place. When the tests were finished, the surfaces of the samples were cleaned and reflectance measurements were carried out. Five cycles were performed and the results are summarized in Table 6.

During the thermal cycling of the Al-Si$_y$O$_x$ mirrors, the experimental conditions were very harsh. Two samples cracked, but the properties of the films of all five samples remained intact. When liquid nitrogen is used

for the low temperature test, the ageing can be accelerated and the test period reduced. However, if dry ice and alcohol are available, they are recommended.

In general, degradation rates are very sensitive to temperature. High temperature can cause the mirror performance to degrade rapidly. According to the recommendation made by Masterson et al. (1983) high temperature exposure must not exceed 80°C. The objective of temperature tests was to examine the thermal stability and performance degradation of first surface mirrors under high temperature conditions. The four pieces of mirror samples were heated by inserting them into a laboratory furnace kept at 70°C under ambient laboratory humidity. All samples were maintained at the same uniform temperature. At 24 h intervals they were removed from the oven, and the appearance and reflectance were checked and measured. They were then returned to the oven for further treatment. No detectable change in the samples was observed after thermal treatment for 72 h. Table 7 shows the results of the temperature test.

The exposure to moist sulphur dioxide was conducted for 48 h. The samples were removed from the test chamber at regular time intervals and the appearance and reflectance checked and measured. They were then returned to the chamber for further exposure. The experimental results are given in Table 8. After a 24h exposure, it was found that sample 9-24-3 had first shown very obvious corrosion (some transparent small holes on it). Its reflectance decreased also, even though a thicker Si$_y$O$_x$ layer (2600Å) was deposited on its surface. This may be accidental and related to the preparation processes of the batch containing sample 9-24-3.

For saltwater immersion, the samples were withdrawn from the salt solution at 24h intervals, rinsed with distilled water, and dried. Their appearance was

Table 9. Reflectance after immersion in saltwater solution

Sample	Thickness (Å)		Reflectance ρ_s				Comments
	Al	Si$_y$O$_x$	Previous	Immersion time			
				24 h	48 h	72 h	
10-07-3	1257	2850	0.884	0.884	0.885	0.884	
10-01-3	980	1557	0.845	0.845	0.847		local corrosion
09-14-3	1247	2361	0.879	0.878	0.881	0.880	
07-16-3	1000	2200	0.868	0.868	0.869	0.868	

Table 10. Reflectance after abrasion tests

Sample	Thickness (Å) Al	Thickness (Å) Si$_y$O$_x$	Strokes Dry	Strokes Wet	Reflectance ρ_s Before	Reflectance ρ_s After
03-24-1	1300	2570	200		0.865	0.865
04-06-2	1000	2500		200	0.866	0.865
07-14-1	1200	2100	200		0.873	0.874
07-06-3	1050	2000		200	0.873	0.874

checked and the reflectance measured. Table 9 summarizes the results of the salt water immersion test. After 72h immersion, there was no drop in reflectance nor change in the appearance of three samples, but noticeable corrosion took place at a localized area of sample 10-01-3 after 24h immersion (see Fig. 4). On the corroded area, the Al reflecting film disappeared. However, corrosion was not observed on the rest of the sample, including its edges. Therefore, it was determined that the local corrosion of sample 10-01-3 resulted from defects of the Si$_y$O$_x$ layer, maybe because the layer was not thick enough.

For the abrasion tests, each sample surface was wipped 200 times with a dry cloth and 200 times with a wet one. No obvious change of appearance or reflectance of the tested samples occurred. The experimental results are listed in Table 10. Table 11 shows a summary of the ageing tests for the Al mirrors with SiO$_2$ protective film.

6. ANALYSES AND DISCUSSIONS OF EXPERIMENTAL RESULTS

6.1 Characteristics of the Si$_y$O$_x$ film

The protective layer over the reflecting film is vital to the service life of first surface solar mirrors. Although an evaporated Al film can grow a transparent protective layer of natural oxide film (Al$_2$O$_3$) with a thickness of about 40 Å in air, as shown by Hass et al. (1982), this rather thin oxide film is unable to prevent the reflecting properties of the film from degrading under severe weathering conditions and frequent cleaning. For example, the outdoor weathering exposure test indicated that in an anodized aluminum foil with a 3-4 μm oxide film sealed by the hot water method, degradation was prevented for a short period. However, degradation occurred after 2-3 months (Cong et al., 1990). A hard and transparent protective layer is definitely needed for Al first surface solar mirrors.

As commented by Hass et al. (1982), Si$_2$O$_3$ films make excellent protective coatings because they adhere strongly to Al and harden rapidly by further surface oxidation when exposed to air. Below 300 nm, a Si$_2$O$_3$ film shows rather high absorptance, as shown by Hass et al. (1982). However, this does not influence the reflection of the mirrors used in the solar spectrum (350-2500 nm, $M = 1$).

The composition and optical properties of the Si$_y$O$_x$ layer depend greatly upon the evaporation conditions:

deposition rates and oxygen pressure. To produce a Si$_2$O$_3$ film with negligible absorptance in the near UV, visible, and near IR, low deposition rates (1 to 3 Å/s) at a rather high oxygen pressure ($\sim 10^{-4}$ Torr) must be used in order to produce Si$_2$O$_3$ as the main stoichiometry.

To determine the absorption of the Si$_y$O$_x$ layer, we deposited only the Si$_y$O$_x$ film on the slide glass sheet surface, then measured and compared the transmittance before and after the film was deposited. From Fig. 3 we can see that the Si$_y$O$_x$ layer produced by this deposition has a very high transmittance and no obvious absorption in the solar spectrum range.

The type of surface structure obtained, whether single-crystal, polycristalline, or amorphous, depends on the substrate temperature and deposition rate (Khan, 1970). From X-ray analyses, reactively evaporated Si$_y$O$_x$ film with high oxygen pressure at a low deposition rate showed an amorphous structure (Chen et al., 1992).

If low oxygen pressure is fed to the evaporator or if the deposition rate is high, the Si$_y$O$_x$ film produced reveals high absorptance for all wavelengths shorter than 500 nm and has a yellow appearance, as discussed by Hass (1982). Similar results occurred in the present experiment.

It is important to clarify some aspects of the composition of the protection film Si$_y$O$_x$. Ritter (1962, 1966, 1972) considered that the evaporation of SiO under similar conditions as ours, produces a film composition of 1.5 oxygen atoms for 1 Si atom (if the reaction were complete, the ratio would be 2:1). An easy way to express this ratio (1.5:1) is by using the Si$_2$O$_3$ formula. The infrared spectra of these films present shift and wider absorption bands than the SiO$_2$ bands (Pliskin and Lehman, 1965). This is due to porosity and an oxygen deficiency, so the structure of the film has many non-bridging, dangling bonds ($\equiv$Si$-$O$\cdot$ $\cdot$Si$\equiv$ instead of $\equiv$Si$-$O$-$Si$\equiv$), which can absorb more oxygen when it is exposed to the atmosphere or if there is water vapor. Because the oxidation process is in fact a surface phenomenon, this oxygen absorption is accomplished only on the surface of the film. In summary, the deposition rate of the Si$_y$O$_x$ film and oxygen pressure have a great influence on the reflectance of Al-Si$_y$O$_x$ first surface mirrors and on the composition of the Si$_y$O$_x$ film.

6.2 Characteristics of the SiO$_2$ film

As discussed before, another alternative for aluminum first surface solar mirrors is the Al-SiO$_2$ films. As commented by Hass et al. (1982), SiO$_2$ also forms a hard and durable coating on Al that is nonabsorbing in the visible and UV down to below 200 nm. A deposition rate of 400 Å/min and a thickness of about 3200 Å are recommended. With these characteristics the specular reflectance is 0.89. If the thickness varies, the reflectance changes a little.

6.3 Influence of deposition rates and thicknesses of Al films on the reflectance of the mirrors

In order to get high reflection, a high deposition rate of the Al film is recommended by Hass et al.

Table 11. Results of accelerated ageing tests of Al-SiO$_2$ first surface mirrors

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Reflectance ρ_s Before	After test 24 h	48 h	72 h	Comments
NaCl solution	10-15-93-2	970	2070	no	0.854	0.856	0.856	0.857	Very few and small
immersion, 5%	11-17-93-2	1208	2800	no	0.868	0.871	0.870	0.866	holes
(w/w) at RT	11-17-93-3	1208	2800	yes	0.873	0.874	0.874	0.870	
	01-14-94-2	1253	3200	no	0.881	0.882	0.880	0.877	
	12-09-93-3	1420	3290	yes	0.875	0.875	0.873	0.873	
	01-18-94-1	1524	3300	yes	0.883	0.882	0.880	0.876	Very few local corrosion

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Before	6 h	24 h	48 h	Comments
Exposure to moist	10-13-93-3	1000	2000	no	0.861	0.861	0.860	0.861	Very few edge corrosion
sulphur dioxide	10-15-93-3	970	2070	no	0.861	0.861	0.861	0.862	
at RT	01-14-94-3	1253	3200	yes	0.884	0.884	0.884	0.884	
	01-12-94-3	1580	3227	yes	0.887	0.888	0.888	0.888	
	12-14-93-1	1615	3283	no	0.889	0.888	0.888	0.888	
	03-03-94-2	1420	3550	yes	0.884	0.884	0.884	0.884	
	02-22-94-3	1455	3664	yes	0.887	0.886	0.886	0.885	

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Before	3 weeks	Comments
Humidity test,	05-11-93-1	1120	1618	no	0.859	0.857	
100% RH at	05-11-93-2	1120	1618	no	0.856	0.853	
RT	05-13-93-1	1134	2320	no	0.866	0.864	
	09-08-93-1	1050	2541	no	0.872	0.869	
	09-08-93-2	1050	2541	no	0.868	0.869	
	08-17-93-1	1122	2636	no	0.856	0.854	
	05-06-93-1	1137	2982	no	0.889	0.887	

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Before	72 h	Comments
Temperature test,	03-11-94-2	1530	2650	no	0.876	0.875	
70°C	01-14-94-1	1253	3200	yes	0.876	0.879	
	02-22-94-2	1455	3664	yes	0.887	0.887	
	03-09-94-2	1450	3840	yes	0.884	0.884	

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Before	6 cycles	Comments
Thermal cycling	03-11-94-2	1530	2650	no	0.875	0.876	
−50°C ↔ 50°C	01-14-94-1	1253	3200	yes	0.879	0.879	
	02-22-94-2	1455	3664	yes	0.887	0.887	
	03-09-94-2	1450	3840	yes	0.884	0.883	

Test	Sample	Thickness (Å) Al	SiO$_2$	Deposition method of SiO$_2$ film, with O$_2$	Before	400 wipes	Comments
Abrasion	11-30-93-3	1200	2500	no	0.851	0.852	
	03-11-94-1	1530	2650	no	0.874	0.875	
	03-03-94-3	1420	3550	yes	0.885	0.886	
	03-17-94-1	1515	3167	yes	0.881	0.881	

(1982) and Ritter (1975). However, one other researcher believes that the deposition rates of Al film do not have any detectable effect on the reflectance by vapour-deposited aluminum (Griffin, 1980). To determine whether the deposition rate of the Al film is an important consideration with respect to reflectance we have prepared some mirror samples deposited at high and low deposition rates separately and then measured their reflectance. The results of this study are summarized in Table 1. From these, we concluded that a high deposition rate of the Al film is important and necessary in order to obtain high reflection of the mirrors.

Regarding the thickness of the Al film, Table 1 shows that there is no obvious reflectance dependence on its thickness, if the film thickness is above 1000 Å. That is, a thickness of or above 1000 Å for Al films possesses all of the reflectance for first surface mirrors.
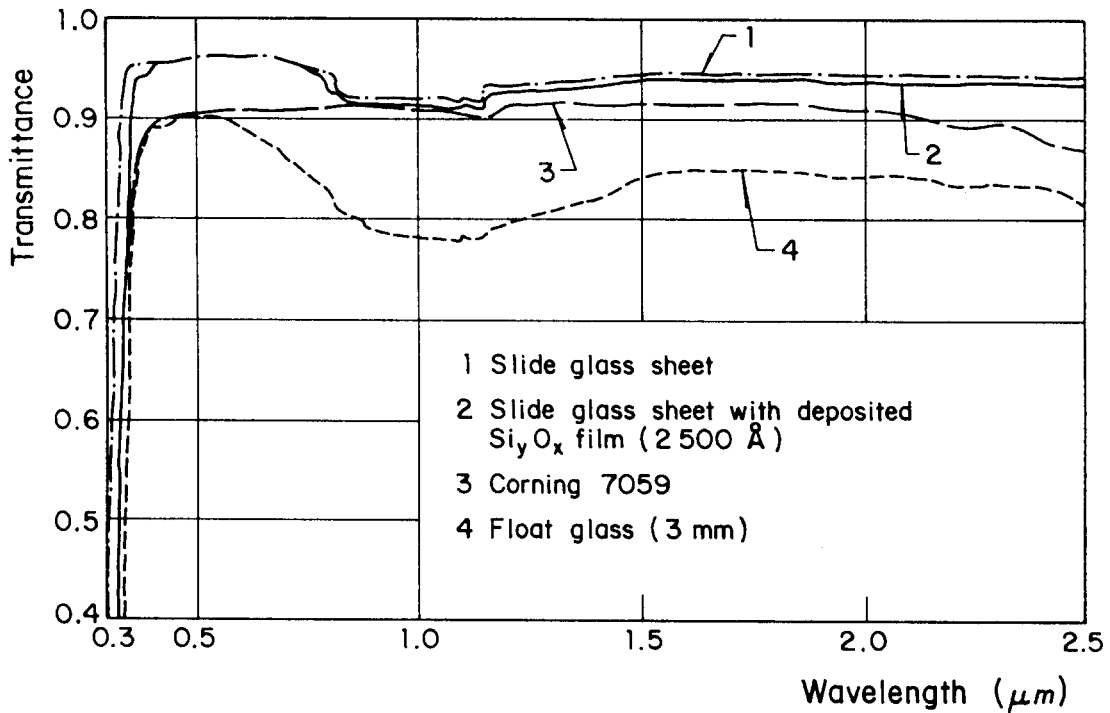
Fig. 3. Transmittance of three kinds of glass.

6.4 *Optimum thicknesses of* Al *and* Si_yO_x *films*

Considering optical properties, depositing time, stress and production cost of the mirrors, the choice of optimum thicknesses of Al and Si_yO_x or SiO_2 films has been studied. From Table 1 the reflectance of the Al film did not increase further if the film thickness was over 1000 Å, therefore, the thickness of the Al film with 1000 Å is suitable for the reflecting layer of the solar mirrors. Considering the Si_yO_x film, it must be thick enough to protect the Al film from corrosion and abrasion, but not so thick that it will reduce the reflectance of the mirrors. The experiment showed that the Si_yO_x film with ~2500 Å thicknesses has a good protective function and high transmittance in the solar spectrum range. For the SiO_2 film, the experimental evidence showed that a thickness of about 3200 Å has the higher transmittance and enough protective function against abrasion.

7. CONCLUSIONS AND SUGGESTIONS

From the analyses of the above experimental results of first surface solar mirrors, the following conclusions can be drawn:

• The Al first surface mirrors with a Si_yO_x or SiO_2 protection film possess high specular reflectance (0.89) and high environment stability. They have proven to be promising reflecting materials and to be very good candidates for solar energy applications.

• Si_yO_x and SiO_2 films are key materials for Al- Si_yO_x and Al-SiO_2 first surface solar mirrors. They have shown very good optical properties and protective

effects. The Si_yO_x film presented an amorphous structure, its stoichiometry is SiO, Si_2O_3 and SiO_2; but the predominating structure is Si_2O_3.

• In order to obtain high reflectance of the mirrors, a high deposition rate for Al and a low deposition rate (3 Å/s or lower) with high oxygen pressure for SiO are very important and necessary. For SiO_2 a rate of about 7 Å/s (420 Å/min) is recommended. The reflection characteristics of protected Al mirrors depend strongly upon the conditions under which the Al and SiO or SiO_2 are evaporated.

• An Al film of about 1000 Å thickness is suitable for the first surface mirrors. To effectively protect the Al reflecting film, a Si_yO_x film of the order of 2500 Å thickness or a SiO_2 film of about 3200 Å thickness is recommended.

• In the accelerated ageing tests, almost all corrosion phenomena observed took place only at a few localized sites of some of the tested mirror samples, for example, 09-24-3, 4-1-1, and 10-01-3. These samples may be considered exceptional. Most of the tested samples were intact. The above facts indicate that the ability of the mirror to resist corrosion may be related to the preparation process of the Si_yO_x (or SiO_2) layer beside the thickness of the layer. Si_yO_x (or SiO_2) has no problem in resisting corrosion as protective material, but certain improper deposition processes of the Si_yO_x (or SiO_2) layer or accidental factors (for example, introduction of impurities, poor uniformity of the film thickness, pinholes or porosity, high deposition rate, incomplete substrate cleaning, etc.) can cause the defects in the Si_yO_x (or SiO_2) layer which lead to

Fig. 4. Photograph of sample 10-01-3 after 24 h immersion showing corrosion.

corrosion. Although all mirror samples were manufactured using the same materials, a few of the samples showed a very localized corrosion.

• The results of accelerated ageing tests have shown that no edge corrosion or edge degradation occurred on the tested mirror samples. Between Al film, Si_yO_x (or SiO_2) film and the glass surface, a very compact and strong bonding existed. Special paints for edge-protection may be unnecessary for the future practical utilizations of such mirrors.

• Oil contamination of the substrate surface from diffusion and mechanical pumps is detrimental to the mirror properties and should be avoided, as shown by Almanza *et al.* (1992b). Besides, cleanliness of the substrate surface would produce good adherence of the Al film to the substrate as well as the reduction or complete elimination of corrosion.

• In the present study, different kinds of glass (float glass, slide glass, Corning 7059 glass sheet, etc.) were used as substrates for Al-Si_yO_x first surface solar mirrors. After accelerated ageing tests, no detectable difference in their properties was found. This study has indicated that a variety of glasses are suitable for manufacturing Al-Si_yO_x first surface solar mirrors. If float glass is employed as the substrate, it is recommended that the Al film be deposited on the non-tin surface. The tin surface can easily be detected by an UV mineralight lamp.

• Aluminum mirrors have higher reflection in the UV range than silver mirrors, Drummeter and Hass (1964). Therefore, they are the best mirrors for detoxification processes when UV is used in solar concentrators.

• Over 100 mirror samples were manufactured under different conditions. They were compared with other mirrors used in solar concentrators like the ECP-305 (3M) and a second surface mirror from Flachglass. The degradation in all the mirrors under the different tests, on the average, was 1–2%.

• In a recent paper published by Schissel *et al.* (1994) testing the ECP-305 mirror under different conditions, a tunneling effect (delamination or exfoliation of silver or aluminum from the substrate) was found when the mirror was exposed to high humidity conditions. However, they have found a method to reduce this phenomenon as discussed in the same paper. The tunneling effect has not been observed in aluminum first surface mirrors up to now under different weathering conditions.

• Another advantage of aluminum first surface mirror is that is possible to use soda-lime silica glass as substrate, instead of an expensive glass like the low iron glass used frequently in second surface solar mirrors.

• It is possible to use flexible substrates such as aluminum, stainless steel, or other metal sheets with a layer of Al_2O_3, SiO_2, or Si_2O_3 in order to get a good adherence between the metal sheet and the aluminum to be evaporated. The sheets must be electropolished before any film evaporation occurs in order to ensure that the smoothness of the metal sheet matches that of float glass because a rough substrate causes light scattering (as discussed by Tao *et al.*, 1994), and the specular reflectance is lower. The advantage of this suggestion is that the metal sheet can be sagged due to its flexibility to form a parabolic trough or another geometric form, avoiding the use of sagged glasses.

• Many important experimental results surrounding Al-Si_yO_x and Al-SiO_2 first surface solar mirrors have been obtained since this research work was performed. However, at present, each mirror sample is limited to a small area. In order to complete this very interesting research project for manufacturing

larger area and increasingly uniform mirrors for practical applications, mainly solar concentrators, linear magnetrons must be used for sputtering deposition. In a future stage, we will start with this technique. Two published progress reports provide more details (Chen et al., 1992, 1993).

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