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CHEMICAL VAPOR DEPOSITION OF REFRACTORY METAL REFLECTORS
FOR SPECTRALLY SELECTIVE SOLAR ABSORBERS

MASTER

Co-Principal Investigators:

B.O. Seraphin
G.E. Carver
Optical Sciences Center
University of Arizona
Tucson, Arizona 85721

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ABSTRACT

Three methods are described to fabricate by chemical vapor deposition (CVD) molybdenum films which rival conventional mirror materials in their infrared reflectance. With an absolute reflectance of 97.4% at 10 μm , these "Super Molybdenum" films reflect better than any other molybdenum film previously reported. When deposited in the presence of oxygen, films of a reduced reflectance over the solar emission range result. If passivated and antireflected by a Si_3N_4 layer, such "Black Molybdenum" films are characterized by a solar absorptance value in excess of 90% and a thermal emittance value of 11% at 500 C. No deterioration of these values has yet been observed in ongoing tests after 1000 hours exposure to 500 C in a 1 Torr vacuum. Stacks containing Super Molybdenum as the reflector and amorphous silicon as the absorber have thus far survived 1000 hours in open air at 500 C.

TABLE OF CONTENTS

ABSTRACT	i
I. INTRODUCTION	1
II. PRODUCTION OF HIGHLY REFLECTIVE MOLYBDENUM THIN FILMS	4
II.1 Pyrolytic Decomposition of Molybdenum Carbonyl	4
II.2 Post-Deposition Treatment	4
III. CHARACTERIZATION OF FILMS	6
III.1 Optical and Electrical Properties	6
III.2 Structure and Composition	7
IV. THE CHLORIDE PROCESS	9
IV.1 Process Control	9
IV.2 Results from the Chloride Process	9
V. THE PRODUCTION OF BLACK MOLYBDENUM	11
V.1 Thin Film Deposition	11
V.2 Post-Deposition Anneal	11
VI. MOLYBDENUM FILMS IN PHOTOTHERMAL CONVERTERS	14
VI.1 Stack Fabrication	14
VI.1.1 Changes in stack fabrication	14
VI.1.2 Identification of failure modes	14
VI.2 Lifetime Testing	16
VI.2.1 Reflector failure mode	16
VI.2.2 Absorber failure mode	17
VI.2.3 Barrier failure mode	18
VI.3 Lifetime Tests With Black Molybdenum	19

VII. SUMMARY	20
VIII. ACKNOWLEDGEMENTS	21
IX. APPENDIX	22
<i>Publications in the Open Literature</i>	

CVD Molybdenum Films of High Infrared Reflectance

G.E. Carver

*Chemical Vapor Deposition of Thin Semiconductor Films
for Solar Energy Conversion*

B.O. Seraphin

*Chemical Vapor Deposition of Spectrally Selective Surfaces
for High-temperature Photothermal Conversion*

B.O. Seraphin

*Chemical-Vapor-Deposited Molybdenum Films of High Infrared
Reflectance*

G.E. Carver and B.O. Seraphin

CVD Molybdenum Thin Films in Photothermal Solar Converters

G.E. Carver

*Chemical Vapor Deposited Molybdenum Films for Use in
Photothermal Conversion*

G.E. Carver, D.D. Allred, and B.O. Seraphin

CVD Molybdenum Films of High Infrared Reflectance

G.E. Carver and B.O. Seraphin

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I. INTRODUCTION

We report here the progress made on the chemical vapor deposition (CVD) of refractory metal films for use in photothermal solar energy converters during the period May 1, 1978 to April 30, 1979. In order to retain the energy absorbed from the incident radiation and pass it along to the thermodynamic cycle, reradiation losses from the converter surface must be minimized by reducing its infrared emittance. The necessary high infrared reflectance must be sustained over long periods of time at temperatures of sufficient Carnot efficiency. On both counts - high infrared reflectance and long lifetime at elevated temperatures - thin films of refractory metals have considerable promise.

Our work under this contract is aimed at the realization of this promise. During an initial two-year phase of the program, completed early in 1978 at the beginning of this report period, we learned to make thin molybdenum films reproducibly by CVD that surpass in their infrared reflectance all molybdenum films deposited in a practical manner by sputtering or evaporation. At the same time, we established the possibility of integrating the refractory metal reflector into a continuous CVD sequence of converter fabrication. We thus combined the high thermal stability of the refractory metal with the advantages of a method that can easily be expanded into economic large-scale manufacture.

At the beginning of this reporting period, we prepared films of 85% reflectance at $10\text{ }\mu\text{m}$ routinely and reproducibly. The most significant result of last year's work lies in post-deposition treatments which raise reflectance levels to values that rival the reflectance of conventional mirror materials. By outgassing the previously deposited molybdenum films at temperatures above $750\text{ }^{\circ}\text{C}$, we increased their infrared reflectance to more than 97% absolute, thereby competing with the reflectance of aluminum mirrors in that spectral range. The process is simple, fast, and reproducible. This significant result combines in our films the temperature durability of a refractory metal with the desirable high infrared reflectance of the more conventional

mirror materials such as aluminum. After the post-deposition treatment, these "Super Molybdenum" films surpass in their infrared reflectance that of any other molybdenum film reported in the literature or in technical reports.

In tracing the dramatic increase of the reflectance through the anneal, we observed a correlation to the content of molybdenum oxide, carbide, and/or oxycarbides that are inherently incorporated into the growing film during the deposition. As the anneal lowers this content, the films undergo structural transformations, and their grain size increases. It is another significant result of last year's work that we began to establish a qualitative understanding of the influence of impurities, structure, and grain size onto the optical and electrical properties of molybdenum films. Such an understanding is a prerequisite to an optimized process control in their fabrication.

In utilizing this increasing control of the process parameters, we have also learned that deposition in certain areas of the Mo-C-O phase diagram results in films of considerable absorption in the solar emission range. When antireflected and passivated with a layer of Si_3N_4 , these "Black Molybdenum" films have solar absorptances approaching and in some cases exceeding 90%. This promising performance in films that have passed through an anneal at temperatures in excess of 800 C makes black molybdenum a candidate for a very simple, all-CVD spectrally selective surface of high temperature durability.

As planned in the original proposal, we have subjected our films to rigorous lifetime testing at 500 C in air and have analyzed their compatibility with layers above and below during fabrication and operation at high temperatures. We have identified a number of failure modes that can be bypassed in the design and fabrication of the stack. The results of these tests are preliminary at this point. It can be stated, however, that highly reflecting "Super Moly" as well as "Black Moly" are compatible with their neighbors during the steps of stack fabrication as well as during subsequent operation.

The rapid progress during this past year has been documented in a number of publications, most of them in refereed journals. We have attached

reprints of these publications to this report. Consequently, we could afford in this Annual Report a conceptual description of our work that highlights the principal accomplishments and places them in perspective to previous work by us and by others in the area. The reader interested in the full details of our work is directed to the Appendix where several open-literature publications present these details in the proper manner. The reader also finds in these reprints the references to other work that are omitted from this Report.

The testing of the high-temperature lifetime and compatibility of our reflector films and stacks are not treated in sufficient detail in the publications. We consequently describe this part of our work more fully in Chapter VI of this Annual Report.

II. PRODUCTION OF HIGHLY REFLECTIVE MOLYBDENUM THIN FILMS

During the past year, use of Chemical Vapor Deposition (CVD) resulted in the production of molybdenum thin films of high infrared reflectance. At this writing, the most reflective films have been prepared by three methods, to be discussed below.

II.1 *Pyrolytic Decomposition of Molybdenum Carbonyl*

The first method is based on the thermal, or pyrolytic, decomposition of Mo(CO)_6 . The carbonyl reaction was initially chosen because it proceeds at the relatively low temperature of 300 C, and furthermore does not generate corrosive gases in the process. Previous work by others used the carbonyl reaction at reduced pressures and at higher temperatures. Anticipating the large-scale fabrication required in solar technology, however, we wanted to produce highly reflective molybdenum at a moderate temperature, and under one atmosphere of argon, thereby facilitating future flow-through continuous manufacture. Our present deposition parameters allow for a relatively simple system, which does not require costly vacuum apparatus.

Films deposited under these conditions from the carbonyl were initially limited, however, to a reflectance of only 85% at 10 microns. It is the principal result of last year's work that this value could be substantially improved by a post-deposition treatment described in the next section. At the same time, the reasons for the initially low reflectance levels became apparent.

II.2 *Post-Deposition Treatment*

The moderate reflectance of films deposited with the carbonyl process is substantially increased by subjecting them to a post-deposition, high temperature anneal. The structure and composition of the films are changed during anneal in such a way as to increase the absolute reflectance to 97.4% at 10 μm . This value is within 0.7% of the reflectance of supersmooth

bulk molybdenum. Figures 1 and 2 show that the anneal must last from 30 minutes at 750 C to 5 minutes at 1000 C in order to produce films of the near-bulk reflectance.

FIG. 1. Relative reflectance, at $10\ \mu\text{m}$, of CVD molybdenum films plotted against the temperature of a 5-min anneal.

FIG. 2. Relative reflectance, at $10\ \mu\text{m}$, of CVD molybdenum films plotted against the duration of anneal at 750°C .

The spectral dependence of the infrared reflectance is plotted in Figure 3 as measured with an accuracy of 0.1% by J.H. Bennett at the Naval Weapons Center, China Lake, CA. The reflectance of a molybdenum film which was sputtered in ultrahigh vacuum at China Lake is shown for comparison.

Figure 3. The absolute reflectance, from 3 to $15\ \mu\text{m}$, of super-smooth bulk Mo, unprotected and passivated CVD Mo after anneal, and sputtered Mo.

The success of the annealing process is not dependent on a reducing atmosphere. Anneals of reflective films from the carbonyl process in either He + 10% H₂ or pure He have produced similar optical results. Deposition from the carbonyl plus anneal in either reducing or non-reducing atmospheres compose our first two methods of producing "Super Molybdenum". Differences between the two methods will be brought up in the following sections.

III. CHARACTERIZATION OF FILMS

III.1 Optical and Electrical Properties.

While discussing optical reflectance in the infrared, it must be emphasized that the high infrared reflectance of molybdenum does not extend into the visible. In fact, molybdenum reflects on the average less than 60% of visible radiation, and absorbs about 37% of solar radiation. This low reflectance in the visible, together with the high infrared reflectance can be useful in photothermal converters.

Changes in electrical conductivity accompany the enhancements in reflectance which we observe during anneal. Some representative data are shown in Table I.

TABLE I. Thickness, electrical conductivity at 20 °C, and absolute reflectance at 10 μ m of an as-deposited film, an annealed film, and supersmooth bulk molybdenum.

Sample	Thickness (μ m)	Conductivity at 20 °C ($\mu\Omega$ cm)	Absolute reflectance at 10 μ m (%)
As-deposited	0.154 ± 0.006	250 ± 25	85 ± 1
Annealed	0.134 ± 0.007	9 ± 2	97.4 ± 0.1
Bulk Mo	...	5.7^a	98.1 ± 0.1

^aHandbook of Chemistry and Physics, 52nd ed. (Chemical Rubber, Cleveland, 1971), p. E-72.

Changes in the optical and electrical properties have been correlated by our investigations to changes in structure and composition of the films which are discussed in the next section. It is the second principal result of last year's work that this relationship between optical and electrical properties on the one hand, and structure and purity on the other have been quantitatively and reproducibly established.

III.2 *Structure and Composition*

Determination of the structure by X-ray diffraction established that films deposited from the carbonyl process are face-centered cubic (fcc). Auger spectroscopy showed that they contain only approximately 62 ± 15 atomic percent molybdenum; while they are composed of 100 Å wide grains. The small grain size is typical of metals deposited at temperatures far below their melting point. The fcc phase is likely stabilized by carbon and oxygen impurities, which make up the remaining atomic fraction of the as-deposited film, resulting from the incomplete decomposition of molybdenum carbonyl at 300 C. All three properties - structure, impurities, and grain size - influence the reflectance of the film.

Figure 4 shows the effect of annealing on the composition and structure, as well as on the reflectance of the films. Carbon and oxygen levels drop by an order of magnitude, which permits the film to go through a series of structural changes. The existence of different crystal structures within the films is indicated immediately beneath the horizontal axis of Figure 4. At the same time, the grain size increases by a factor of 50 - 100. The resulting Super Molybdenum film is therefore composed of relatively pure, large grained material which is bcc.

It is significant that anneals of films from the carbonyl process under either He or H₂ or under pure He have resulted in films with optical properties which are similar. The same changes in grain size, composition,

and phase are observed after anneal in either atmosphere. Annealing under H_2 allows for the outgassing of carbon and oxygen as either CO , CO_2 , H_2O , or CH_4 . Annealing under He allows for only the CO and CO_2 outgassing routes. A film containing only oxygen as an impurity would therefore not outgas during a H_2 anneal. This fact is of importance concerning the long-term stability of "Black Molybdenum", which is discussed below.

It is evident that the anneal has changed the phase, the impurity level, and the grain size of the films. Work presently underway will identify how important each of the three effects are in changing the reflectance. Since all three changes during annealing of films from the carbonyl process occur at the same time, another deposition system was needed for depositing films which, for example, have small grain size with no impurities. The hydrogen reduction of molybdenum pentachloride was chosen. This system has been brought on line and is discussed in the next section.

Figure 4. Relative reflectance (at 10 μm), C and O content as determined by Auger spectroscopy, and crystal structure as determined by XRD, of CVD molybdenum films plotted against the temperature of a five minute anneal.

IV. THE CHLORIDE PROCESS

IV.1 *Process Control*

As an alternative to the carbonyl process, molybdenum can also be deposited by reducing MoCl_5 with hydrogen. The reaction proceeds above 500 C and evolves HCl gas. In addition to the corrosiveness of this by-product, MoCl_5 tends to oxidize and is therefore easily contaminated with oxychlorides (for example, MoOCl_4 , MoO_2Cl_2). The oxychlorides are simultaneously reduced during deposition, and can lead to the incorporation of oxygen within the growing film. As a consequence of the need to both contain the HCl and to protect the MoCl_5 against oxidation, the chloride system must be well sealed. The system was therefore constructed with high purity ground glass joints and stopcocks. Bringing the chloride process on line is the third principal accomplishment of the past year's effort.

IV.2 *Results from the Chloride Process*

Initial depositions from MoCl_5 were done at 750 C with an argon:10% H carrier gas. Molybdenum chloride was carefully loaded into the reactant gas generator under N_2 in a glove box. Valves at the inlet and outlet of the generator were closed before removing the generator from the glove box. After connecting it to the chloride system, both the inlet and outlet lines to the generator were pumped out and then backfilled with carrier gas before the generator's valves were opened. These precautions probably kept the MoCl_5 nearly as pure as it was upon shipment from the manufacturer. Films deposited at 750 C exhibit reflectance levels which match the reflectance of fully annealed films from the carbonyl process. This approach constitutes our third method for producing molybdenum films of near-bulk reflectance. These 750 C deposits also have the same composition, grain size, and crystal structure as the completely annealed films from the carbonyl process.

Proper evaluation of the results from the chloride process permits separation of the optical effects of changes in crystal structure, impurities, and grain size. Knowing the process parameters for direct deposition without subsequent anneal, we could systematically make inferior films by proper change of these parameters, and study the effect on the reflectance. Two examples

can be given at this time. First, if clean MoCl_5 is used during a deposition at 500 C, a pure, but fine grained body-centered cubic (bcc) film results. This allows for an evaluation of the effects of grain boundary scattering. Second, if oxygen is added to either the reactant stream (or to the reactant generator itself) an oxygen contaminated bcc film results. This allows for an evaluation of the effects of impurity scattering and oxygen-molybdenum bonding. Once the effects of grains and oxygen have thus been determined, the result of a change in crystal structure from fcc to bcc, as observed in films deposited by the chloride process may be determined.

V. THE PRODUCTION OF BLACK MOLYBDENUM

V.1 *Thin Film Deposition*

This Report has thus far discussed the optical properties of highly reflective films, which we dubbed "Super Molybdenum", because their reflectance at $10\text{ }\mu\text{m}$ is superior to that of any other molybdenum film reported previously. Even pure bulk molybdenum absorbs 37% of solar radiation. "Black Molybdenum" thin films in the as-deposited state have solar absorptances of about 77%. These films are deposited from the carbonyl in the presence of an oxygen bleed at 300 C. In the as-deposited state, black molybdenum reflects less than as-deposited reflective molybdenum from the carbonyl in both the visible and infrared spectral ranges. As-deposited black molybdenum contains substantial amounts of oxygen, little carbon, is fine grained, and has a monoclinic crystal structure, indicative of MoO_2 .

V.2 *Post-Deposition Anneal*

Post-deposition annealing in H_2 has increased both the visible and infrared reflectance of Black Molybdenum. During a hydrogen anneal, these films outgas oxygen, presumably as H_2O , and revert to a bcc crystal structure. Several minutes of anneal under H_2 at 1000 C completely outgasses black molybdenum. These fully annealed Black Molybdenum films rival the reflectance of films which are deposited without the oxygen bleed from the carbonyl, and subsequently annealed. Our interest in Black Molybdenum lies in the optical properties which are attained by a partial anneal. We have found that the infrared reflectance of Black Molybdenum rises faster than the visible reflectance during anneal. Therefore, after an anneal of about five minutes at 800 C, we obtain a single layer which exhibits respectable selectivity. Further, the optical constants of our CVD Si_3N_4 match Black Molybdenum well enough to enable an overcoat of the nitride to anti-reflect the black film over a wide band in the visible. The Si_3N_4 film also passivates the Black Molybdenum against oxidation.

Antireflected Black Molybdenum has attained a solar absorptance of 0.91 and a thermal emittance, as based on the 500 C blackbody profile, of 0.11. The a and e values of Black Molybdenum and Super Molybdenum are shown together with reflectance curves in Table II and in Figures 5 and 6.

TABLE II. a and e of Molybdenum from the Carbonyl Process

Sample	a (% of Air Mass 2)	e (500 C)	Curve # in Figs. 5,6
Annealed reflective Mo	0.37	0.03	1
As-deposited Black Mo	0.77	0.44	2
Annealed Black Mo (770 C, 7 min.)	0.74	0.08	3
Anti-reflected, annealed Black Mo	0.91	0.11	4

Figure 5. Distorted λ -plot of the solar absorptance a of a set of thin molybdenum films. See Table II for the different treatment of the samples.

Figure 6. Distorted λ -plot of the thermal emittance ϵ for a blackbody temperature of 500 C for the sample set of Figure 3.

We are optimizing the process parameters of Black Molybdenum with respect to α and ϵ by making systematic changes in the oxygen bleed, anneal temperature, and length of anneal. Our analysis of which film properties dominate the infrared reflectance of reflective molybdenum will aid in understanding the infrared reflectance of Black Molybdenum. Our optimization program will lead to an understanding of the solar absorptive mechanism in Black Molybdenum. Existing data for Black Molybdenum establishes it as a candidate single layer, highly selective converter of promising thermal stability.

VI. MOLYBDENUM FILMS IN PHOTOTHERMAL CONVERTERS

VI.1 *Stack Fabrication*

VI.1.1 *Changes in Stack Fabrication*

The first photothermal stacks fabricated at the Optical Sciences Center were composed of polycrystalline silicon and silver films deposited on oxidized stainless steel substrates. Subsequent work has replaced polycrystalline silicon with amorphous silicon and silver with molybdenum, with both layers deposited by CVD. Consequently, the new configuration is an absorber-reflector tandem as follows:

Absorber of solar radiation:	1.5 μm of a-silicon
Passivation:	SiO_2
Infrared reflector:	as-deposited molybdenum
Barriers:	<div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> $\diagup$ $\diagdown$ </div> <div> SiO_2 native oxide </div> </div>
Substrate:	stainless steel

This multilayer stack served as a vehicle for initial lifetime and compatibility testing. The stack was exposed to air for 1000 hours at 550 C and a number of failure modes were identified. Subsequent stacks of a modified design then eliminated these failure modes recognized in the initial tests, and withstood successfully similar tests without deterioration, as described below.

VI.1.2 *Identification of Failure Modes*

The following mechanisms were observed to contribute to the deterioration of the performance of the stacks described above:

- a. Thermal expansion mismatch can cause the substrate and thin film layers above it to expand at different rates, leading to cracks and peeling in the stacks.

- b. Oxidation of the molybdenum can form a surface layer that evolves out of the film.
- c. Outgassing of the molybdenum can cause the layers above the molybdenum to flake off by the thrust of the effused gas.
- d. Pinholes in the barrier layers can lead to oxidation of the molybdenum underneath.
- e. Crystallization of the a-silicon during lifetime testing causes a change in the material's volume. This causes cracking in this layer and permits the molybdenum below to oxidize.

In order to determine the relative importance of these various failure modes and to suggest means of bypassing them, we designed tests to evaluate problems in each layer of the converter stack. The configuration now used in these follow-up tests was:

Absorber of solar radiation:	1.5 μm of a-silicon
Passivation:	750 Å of Si_3N_4
Infrared reflector:	as-deposited or annealed molybdenum
Substrate:	quartz

No problems were encountered during the production of these all-CVD stacks, proving the compatibility of the fabrication process.

VI.2 *Lifetime Testing*

Two sample sets were deposited using the above configuration on quartz, one with as-deposited molybdenum from the carbonyl, and the other with completely annealed molybdenum. Quartz was used as a substrate in order to avoid the thermal expansion mismatch previously encountered when using stainless steel substrates.

These stacks were tested in air at 500 C for over 1000 hours. This lowering of the testing temperature from the 550 C used in previous tests is significant in two ways. First, it lengthens the time required for crystallization of the silicon well beyond the duration of the test. It secondly lowers the temperature below that at which the oxidation of the molybdenum proceeds parabolically. The results of this testing are described in the following sections.

VI.2.1 *Reflector Failure Mode*

The two types of films tested were as-deposited molybdenum and completely annealed Super Molybdenum. For the second form, we expected one advantage and one disadvantage to become effective. Since the Super Molybdenum was more pure, it might be expected to oxidize more readily. But since it had been completely annealed, it was not expected to undergo any further outgassing during the lifetime testing.

After 1000 hours, we observed severe flaking in the stacks containing as-deposited molybdenum, while, in contrast, the stacks with the annealed Super Molybdenum remained intact and retained their original high infrared reflectance. It could be concluded that the flaking is probably related to the long-term outgassing of the as-deposited molybdenum at 500 C, while this failure mode is easily avoided by the use of Super Molybdenum, which undergoes no further change.

VI.2.2 Absorber Failure Mode

After the initial 1000 hours of testing, we used the sample set containing annealed molybdenum to isolate a failure mode associated with the crystallization of the silicon layer. Half of the set was exposed to 675 C in a reducing atmosphere (thereby avoiding oxidation) until the silicon crystallized. The other half remained amorphous. The entire set was then returned to the 500 C test in air. The samples with crystallized silicon exhibited severe reflectance loss within 73 more hours, while the samples with a-silicon remained unchanged.

Since all of these samples had originally withstood 1000 hours, the crystallization of the a-silicon layer clearly is responsible for the failure of the crystallized half of the set. The crystallization probably causes cracks in the silicon and nitride barrier which leads to oxidation of the molybdenum. This failure mode has been completely eliminated by the accomplishments made under a companion contract involving the optical properties of stabilized amorphous silicon. Work under this contract has shown that the intentional doping of a-silicon with carbon can retard crystallization of amorphous silicon for several decades, even if kept at 700 C.

Additional work under the silicon program has shown that with the superior optical properties of a-silicon, the absorber layer need be only as thick as 2000 A. This result is of consequence to the thermal emittance of our stacks, because thinner silicon layers move reflectance interference minima closer to the visible range, as was the case with the 1.5 μm layers used in this test. The low emittance of the molybdenum can then be fully utilized. Since less than 2000 A of silicon is now clearly the optimal thickness, we have subsequently progressed to a next-generation configuration as follows:

Absorber of solar radiation:	< 2000 A carbon-doped a-silicon
Passivation:	Si_3N_4
Infrared reflector:	annealed molybdenum
Substrate:	quartz

By identifying each individual failure mode and by learning how to avoid it, we gradually proceeded to make better and better stacks. Our testing configuration is consequently allowed to evolve as we stabilize each of the component layers by identifying and avoiding successive failure modes.

VI.2.3 Barrier Failure Mode

Small pinholes in the silicon nitride barrier lead to stack deterioration by oxidation of the molybdenum. Previously we had used 750 Å of Si_3N_4 as a molybdenum passivating layer. At the Motorola Inc.'s facility in Mesa, Arizona, Si_3N_4 can be deposited by CVD with a very low pinhole density and a thickness of 1100 Å. We are currently testing molybdenum passivated by:

- a. 1100 Å of Si_3N_4 deposited at Motorola,
- b. 1100 Å of Si_3N_4 deposited at the Optical Sciences Center,
- c. 750 Å of Si_3N_4 deposited at the Optical Sciences Center, as has been used in previous tests as the passivating layer.

The tests conducted thus far at 500 C in air have shown essentially no difference between Si_3N_4 deposited here at the Optical Sciences Center or at Motorola, if equal thicknesses are employed. The tests have simply shown the passivating action of 1100 Å to be superior to that of 750 Å, as is plausible.

We also have deposited complete stacks using carbon-doped amorphous silicon as absorber, and the three different passivating layers just described. Differences in these sets during tests at 500 C in air will determine the role of eventually remaining pinholes in the Si_3N_4 .

A further sample set with no barrier between the molybdenum and the amorphous silicon is being tested at the same time. If this set survives as well as the others, we will conclude that 2000 Å of amorphous silicon itself is sufficient for protecting molybdenum from oxidation. This result will enable us to further simplify our stack configuration.

VI.3 *Lifetime Tests with Black Molybdenum*

Anti-reflected Black Molybdenum, in addition to its superior optical performance, promises to be stable at high temperatures. During the partial anneal, it is exposed to temperatures of 800 C and therefore should not deteriorate rapidly at 500 C. Black Molybdenum, being a partially annealed phase, raises the specter of an additional failure mechanism, however. During lifetime testing, the samples would outgass completely, as we have witnessed in previous lifetime tests with as-deposited molybdenum.

There is one critical difference, however. Black Molybdenum does not contain carbon, and therefore prevents the departure of oxygen in the form of CO or CO₂, as is the case for as-deposited molybdenum. Consequently, one can expect Black Molybdenum to survive lifetime testing, as preliminary tests have actually shown. Two samples of antireflected Black Molybdenum have not changed in either α or ϵ after 1000 hours at 500 C in a vacuum of 1 Torr. This establishes the fact that the partially annealed state of Black Molybdenum is stable over extended periods of time at 500 C without suffering diffusion-related failure modes.

For Black Molybdenum it is possible to use the passivating layer of Si₃N₄ as an antireflective coating. We will use the optimum AR thickness of Si₃N₄ as our passivating barrier, and samples thus made will be tested in oxygen-bearing atmospheres.

VII. SUMMARY

As of May 1, 1979, the state of our program can be summarized as follows:

1. We can reproducibly deposit molybdenum films of very high infrared reflectance ("Super Molybdenum") by three different methods;
 - a. Pyrolytic decomposition of Mo(CO)_6 and subsequent anneal in a reducing atmosphere ($\text{He} + \text{H}_2$)
 - b. Pyrolytic decomposition of Mo(CO)_6 and subsequent anneal in a non-reducing helium atmosphere
 - c. Hydrogen reduction of MoCl_5 without post-deposition anneal

With an absolute reflectance of 97.4% at 10 μm , Super Molybdenum films rival the reflectance of conventional mirror materials and exceed that of any other molybdenum film previously reported.

2. Super Molybdenum films are large-grained, of bcc structure, and contain only small amounts of carbon and oxygen.
3. Films deposited from Mo(CO)_6 in the presence of an oxygen bleed show a strongly reduced reflectance over most of the solar emission range. If antireflected and passivated by a thin Si_3N_4 film, the solar absorptance α of such "Black Molybdenum" films exceed 0.90, with their thermal emittance ϵ being as low as 0.11 at 500 C.
4. Rigorous lifetime testing of entire stacks revealed failure modes associated with reflector, absorber, and barrier layers. Once identified, these failure modes were eliminated. Stacks containing Super Molybdenum as the reflector and amorphous silicon as the absorber have thus far survived 1000 hours at 500 C in open air.

5. Antireflected and passivated Black Molybdenum retained values of $\alpha = 0.90$ and $\epsilon = 0.11$ after 1000 hours at 500 C in 1 Torr vacuum. Its performance qualifies Black Molybdenum to be a good approximation to a high-temperature spectrally selective coating.

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IX. APPENDIX

CVD Molybdenum Films of High Infrared Reflectance

G.E. Carver

*Chemical Vapor Deposition of Thin Semiconductor Films
for Solar Energy Conversion*

B.O. Seraphin

*Chemical Vapor Deposition of Spectrally Selective Surfaces
for High-temperature Photothermal Conversion*

B.O. Seraphin

*Chemical-Vapor-Deposited Molybdenum Films of High Infrared
Reflectance*

G.E. Carver and B.O. Seraphin

CVD Molybdenum Thin Films in Photothermal Solar Converters

G.E. Carver

*Chemical Vapor Deposited Molybdenum Films for Use in
Photothermal Conversion*

G.E. Carver, D.D. Allred, and B.O. Seraphin

CVD Molybdenum Films of High Infrared Reflectance

G.E. Carver and B.O. Seraphin

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